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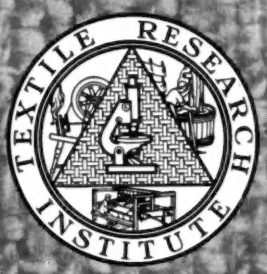

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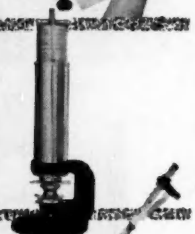

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The Diffusion of Water Vapor through Laminae with Particular Reference to Textile Fabrics

Margaret E. Whelan, Lloyd E. MacHattie, A. C. Goodings,[1] and L. H. Turl[2]

A Contribution from the Defence Research Medical Laboratories, Toronto, Canada

Introduction

THE transfer of moisture from the skin through clothing is an important factor in human comfort. This is true not only in connection with hot atmospheric conditions and the effects of high physical activity but also in relation to cold-weather clothing. Under normal conditions, with a resting subject, insensible perspiration amounts to about 15 g/sq m/hr, and under conditions of exertion or a hot environment the perspiration increases to a value which may be in excess of 100 g/sq m/hr. In principle, the function of perspiration as a factor in body-temperature regulation will be most efficiently achieved if evaporation takes place immediately. Impedance offered by clothing to vapor movement outward will obviously suppress or reduce this form of heat transfer. However, the greater thermal insulation needed for comfort under very cold conditions unavoidably introduces a greater resistance to vapor flow. Under environmental conditions of low temperatures but high relative humidity, condensation of water at points within the clothing may occur, depending upon the thermal gradient and the distribution of impedance to water-vapor transfer. The appearance of such condensate in the clothing may both impair its insulative value and also impose an unwelcome burden of further heat demand upon the body. The diffusion of water vapor through clothing materials is consequently a subject about which quantitative information is most desirable for the proper design both of items of clothing and of clothing assemblies. The present report records the results of a study of water-vapor transfer by the diffusion process through laminar materials, having particular reference to the clothing problem.

The permeability of materials to the passage of water vapor has been a subject of interest in fields other than textiles for some considerable time, but the concern has, in the main, been with impermeability or high resistance as the desirable feature rather than conversely, with ease of movement of water vapor. This difference has an important bearing on the nature and techniques of the study which should be undertaken to provide desirable information. In the field of packaging materials, for example, the experimental methods employed for measuring moisture transfer are in general adapted only to materials of high resistance. This is similarly true of methods which have been used widely on paper, plastic films, and leather. In the case of most textiles, however, the resistances to be measured are low, being of the same order as that of air. This

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fact necessarily requires a different approach to the problem of measurement if results having a reasonable degree of accuracy are to be obtained.

During World War II, the importance was recognized of a more precise knowledge of the water-vapor permeability of textile fabrics than was then available. Investigations were undertaken independently in Canada, the United States, and Great Britain, and some useful information was compiled. Under the stress of conditions existing at that time, however, it was necessary to limit attention to objectives which appeared to be of primary importance for the immediate or early application of results. These objectives included the development of a method of measurement capable of providing values of reasonable accuracy in precise physical units, and applying it to the evaluation of fabrics of particular interest to the armed services. The studies were, however, in no way complete, and left unanswered, or only imperfectly answered, many basic questions such as the role of the fiber in transmitting water vapor and the relative significance of different variables inherent in fabrics. It was recognized that a better understanding of the mechanism of the transmission of water vapor through materials should be sought, and that this greater knowledge could undoubtedly be applied to advantage in the design of fabrics and clothing assemblies.

The work done in Canada during World War II on the permeability of fabrics to water vapor was carried out for the NRC Associate Committee on Aviation Medical Research (Sub-Committee on Protective Clothing), and the results were reported in ACAMR Rept. No. C2655 (SPC Rept. No. 160). The work done in the United States on the problem during the war was carried out by Fourt and Harris, and their findings have since been published [3]. At the time that these earlier studies were in progress in Canada and the United States, information was exchanged between workers engaged on the problem in the two countries. Identical fabrics were subjected to test, and the experimental results obtained showed good agreement. The work carried on independently in Britain at the same time by Pierce, Rees, and Ogden has also since been published [7]. The most comprehensive recent review of the literature on methods of determining the water-vapor permeability of laminae was published in 1950 by Newns [6], working at the British Cotton Industry Research Association, but no description of further studies or results of new experimental work have since appeared from that source.

In 1951 the subject was reopened and included in the textile research program of the Defence Research Board as a matter for further systematic and detailed study. This report describes the work which has now been carried out. For convenience in presentation the report is divided into three parts. The first part deals with the method of measurement and includes results and discussion on the resistance to water-vapor diffusion of external air layers associated with laminar materials. The second part deals with the results of a study of the transmission of water vapor by diffusion through perforated metal plates and mathematical consideration of the problem. The third part is concerned chiefly with the resistance to the diffusion of water vapor offered by fabrics. Also included in this part, because of their value in the analysis of results obtained on fabrics, are some experiments on the water-vapor permeability of layers of impermeable particles and materials in the form of films.

Part I: Method of Measurement

Abstract

Methods employed in the measurement of permeability to water vapor of materials offering high resistance are unsuited for use with textile fabrics. The problem of measurement is reviewed, and it is pointed out that the relationship between the diffusion resistance and the thickness of a fabric is linear but not proportional. A method developed particularly for low-resistance laminae is described and validated, noting the existence and importance of air layers external to the lamina. It is shown quantitatively that the resistance of these layers is reduced by air movement.

The method of measurement of resistance to the passage of water vapor most widely used in connection with [1] and also for leather [4] consists in observing the rate of absorption of moisture by a desiccant in a suitable container when the latter is covered by the material under test and exposed in an atmos-

phere of controlled relative humidity and temperature. Alternatively, water instead of a drying agent may be placed inside the dish and the rate of evaporation of moisture from the dish determined. Results are expressed in grams of moisture transmitted through the material per square meter per 24 hr. Such a method is essentially a comparative one which will determine whether one material is more or less permeable to water vapor than another; only in the case of materials of high resistance will the comparison approach quantitative validity and permit expression of results in precise physical units. This is because the rate of flow of moisture into or away from the weighed container is governed not simply by the resistance of the material under test but also by the resistance of an air layer on either side of the test specimen through which a vapor-pressure gradient exists. By using a solid desiccant in contact with one face of the test specimen, one of the associated air layers can be reduced although not entirely eliminated, and the fact that the contact is partial and not uniform across the whole surface itself introduces a problem in precise measurement. Only where the resistance of the test material is large in comparison with the resistances of the air layers can the rate of transfer of moisture be taken as inversely proportional to the resistance of the material alone. In the case of a textile fabric, the resistance to the passage of water vapor is relatively low and in the large majority of cases is actually less than the resistance of the associated air layers mentioned. Precise, quantitative measurement of the vapor permeability of fabrics therefore necessitates either accurate measurement of other resistances involved in the evaporation rate or some alternative method which effects their elimination from consideration.

Analysis of the Problem of Measurement

The primary objectives in a study of the permeability of fabrics to water vapor are to measure this property in a quantitative manner capable of ready application to clothing problems and to provide an increased understanding of the factors involved and their relative significance.

In diffusion processes, such as gases in gases or salts in solution, it is customary to represent rates of transmission by the "diffusion coefficient," which expresses the amount of diffusing substance that passes per unit time through unit area of the diffusion medium under a unit pressure or concentration gradient. These diffusion coefficients are applicable to homogeneous media (homogeneous in the sense that molecular dispersions are homogeneous) and are useful quantities in describing diffusion behavior in such systems. In the case of fabrics, however, this type of homogeneity does not exist. A fabric is a conglomeration of fibers and air in which the fibers occupy roughly one-third of the total bulk. The individual fibers themselves have diameters of the order of 25 μ. This structural form results in a relationship between thickness of material and its moisture impedance, which though linear is not one of proportionality, a point which will be discussed later in more detail. There is not, therefore, a quantity similar to a diffusion coefficient and possessing merits of constancy that can be ascribed even to those fabrics within a class which differ only in thickness. Moreover, thickness itself is not of importance; the concern is with the permeability or resistance to moisture transfer offered by the fabric as a whole, whatever its thickness may be. It is necessary therefore to consider each fabric individually and ascribe to it some number which is a measure of its vapor-permeable property.

The most useful expression of the water-vapor permeability of a fabric, with respect to the clothing problem as a whole, is in terms of the thickness of a layer of still air which would have an equivalent permeability. It is also an advantage to consider vapor passage through a fabric in terms of its resistance to transmission rather than its conductivity, although the designation in terms of an equivalent layer of still air offers ready translation to either form as may be required. The value of considering vapor transmission in terms of resistance lies in the fact that in dealing with clothing assemblies the resistances of the individual layers are additive. The inverse of the rate of transmission rather than the direct value itself will also later be recognized to be a more useful quantity in the measurement of moisture transmission and the interpretation of results.

Consider the ideal case of water vapor diffusing through still air between two parallel planes of fixed vapor pressures, p_a and p_b. From Fick's law, the resistance of the air space (in units of thickness of still air) is given by

$$R = (DAt/Q)(p_a - p_b) \qquad (1)$$

where Q is the mass of water vapor transmitted in time t through area A, and D is the diffusion coefficient of water vapor in air. If, now, a fabric is introduced at the midplane in the intervening space, the lines of diffusion will, in general, cease to be straight and parallel and will become concentrated in the neighborhood of passageways of least resist-

ance through the fabric. Thus only at some distance away from the fabric will planes of sensibly uniform vapor pressure exist, and only at this distance will the lines of diffusion be parallel and uniformly distributed. If the planes of vapor pressure p_a and p_b are sufficiently spaced for this to be the case, then we may define the resistance of the fabric and air space together as the value given by equation (1) where Q is now smaller than it was, because of the presence of the fabric.

The desire to assign to the fabric and air layers separate values which when added will equal the total resistance just defined cannot be realized without adopting a convention which is to some extent arbitrary. In this paper, the resistance of a fabric or other laminar specimen is taken to be that which remains when there is subtracted from the total a resistance corresponding to unobstructed still air of thickness equal to the air space between planes p_a and p_b but external to the "thickness" of the specimen itself. This is not to imply that the resistance of air layers just outside the defined thickness are not greater than they would be if far removed from any flow-distorting obstacle. Part of the resistance assigned to a fabric arises in air layers outside its defined thickness, and this fact leads to a separation of resistance into two terms, internal and external, which are dealt with more fully later. The matter of defining a suitable measurement of thickness is also taken up in a later section of this report.

Method

In Figure 1 are illustrated the several layers in an arrangement consisting of a fabric or other permeable material covering a vessel such as a crystallizing dish containing water, and situated in an atmosphere of controlled temperature and humidity.

The rate of loss of moisture from the dish is governed by the total resistance to diffusion offered by (1) the air layer inside the dish, (2) the fabric covering the mouth of the dish, and (3) a second air layer through which a vapor-pressure gradient extends some distance outward from the external face of the fabric. The various factors to be considered are designated as follows: p_1 = the vapor pressure at the surface of the water; p_4 = the constant vapor pressure of the external air; R_L = the resistance of the air layer inside the dish; R_m = the resistance of the fabric; R_e = the resistance of the external air layer; Q = mass of water vapor transmitted in time

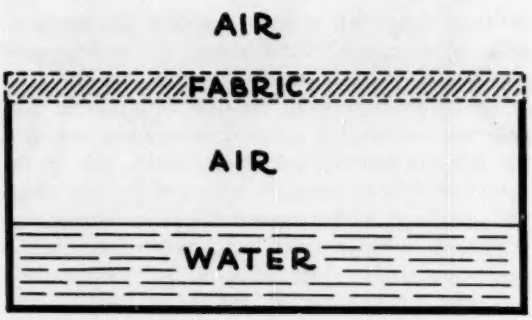

Fig. 1. The rate of loss of moisture from the dish is governed by the total resistance comprising the air layer within the dish, the fabric, and a second layer of air external to the dish (diagrammatic).

t through an area A; U = rate of transfer of moisture per unit area = Q/tA; L = thickness of air layer inside the dish.

The rate U bears a linear relationship to the vapor-pressure difference $(p_1 - p_4)$ and to the inverse of the total resistance.

$$U \propto \frac{p_1 - p_4}{R_L + R_m + R_e} \qquad (2)$$

For the same vapor-pressure difference, therefore, the inverse of the rate is proportional to the total resistance. If a series of tests is carried out in which the distance L between the underside of the fabric and the surface of the water is varied, it is found that this distance has a linear relationship with the inverse of the rate of loss of water vapor, so long as L does not greatly exceed 2 cm. For distances much over 2 cm the rate of loss of water vapor does not fall off according to this relation but rather abruptly becomes almost constant. This peculiarity was previously observed by Langmuir and Schaeffer [5] in their studies of the rates of evaporation of water through compressed monolayers, and is to be attributed to disturbance of the air layer by convection. A similar phenomenon is to be observed in the thermal insulation of an air space and its thickness [2].

For purposes of experimental determination of the resistance of laminae to the diffusion of water vapor, interest is confined to the linear portion of the curve, although for laminae possessing resistances exceeding 2 cm of still air it is nevertheless convenient to use the equivalent thickness of still air in which the linear relation (i.e., without convection currents) may be supposed to obtain.

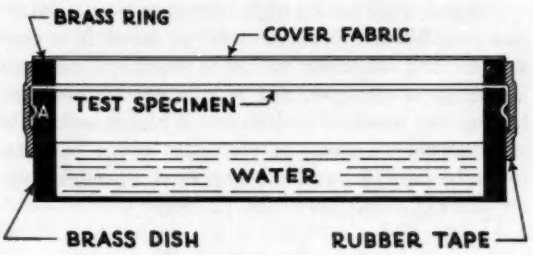

Fig. 2. Experimental apparatus. Sectional view of weighed cell drawn approximately to scale.

Although the relationship between the inverse of the rate of diffusion and L (resistance R_L) is linear when $(p_1 - p_4)$ and R_m remain constant, this does not in itself exclude the possibility that the resistance of the external air layer R_e is subject to change with change in the vapor-pressure drop across it. The question of its constancy will be discussed later, but for purposes of measurement of the resistance of a lamina its influence can be eliminated.

The principle of the method for determining the resistance of a lamina is as follows: Two assemblies similar to the one in Figure 2 are required, one without a test specimen and one including a test specimen. The thickness of still air in each dish is adjusted so that the rates of loss of moisture are the same. Since the rates of evaporation and therefore also the vapor-pressure gradients above the cover fabrics are the same for both assemblies, R_e is the same. If L_1 and L_2 are the thicknesses of the air layers in the two assemblies, R_m = resistance of the cover fabric and R = resistance of the test specimen, then the appropriate relationships for the two assemblies are

$$U \propto \frac{p_1 - p_4}{R_{L_1} + R_m + R_e}$$

and

$$U \propto \frac{p_1 - p_4}{R_{L_2} + R + R_m + R_e}. \qquad (3)$$

Therefore $$R = R_{L_1} - R_{L_2}$$

or, in terms of an equivalent thickness of still air,

$$R = L_1 - L_2 \qquad (4)$$

Since it is impractical experimentally to obtain two assemblies having the same rates as described above, a modified method was actually used. Three assemblies with no test specimens but with differing internal air layers were used to determine the linear relationship between $1/U$ and L. The rate of transfer of moisture from a fourth dish including the test specimen (in which L_2 was known) was substituted in this relationship to find L_1. R was then readily found from equation (4).

Experimental Procedure

In measuring the resistances of laminar materials, six assemblies as shown in Figure 2 were used. Each consisted of a brass dish 2 cm high with an inside diameter of 8.29 cm. Water was placed in the dishes, which had previously been calibrated so that the addition of any known volume of water would give an accurately known distance from the water surface to the top of the dish. The inside of each dish was initially coated with a thin film of a silicone resin (Dow Corning 1107), which was baked on the dishes at 300°F for 10 min. This film prevents the wetting of the sides of the dish above the water level, which otherwise can occur by inadvertent tilting of the dish in handling. In cases where solutions which would normally attack brass were used in place of water, the dishes were coated with a thin film of wax. A brass ring 0.5 cm high and having the same external and internal dimensions as the walls of the dish was covered with an Orlon (Du Pont acrylic fiber) fabric of fairly close weave. In the case of assemblies set up without an unknown test specimen to evaluate the change in rate of loss of moisture with change in the thickness of the air layer within the dish, the ring with its cover fabric was placed, properly aligned, on top of the dish. A strip of electrician's rubber tape was then firmly secured around the outside of the assembly to prevent leakage. In an assembly containing an unknown test specimen, this was inserted between the top of the dish and the bottom of the ring, as illustrated in Figure 2. Rigid test specimens, such as perforated metal plates, were made to the same size as the external dimensions of the dish and ring. Fabrics and films were secured by an elastic band in groove A and then pulled taut prior to sealing at the edges with rubber tape. In order to minimize variability in the resistance of the external air layer which might arise from one period of time to another, the assembled dishes were placed on a turntable which revolved slowly to give a uniform flow of air of about 20 ft per min across the tops of the dishes. The whole equipment was installed in a controlled room operating at $65 \pm 2\%$ R.H. and 70 ± 2°F. After mounting preparatory to an ex-

perimental run, the assembled dishes were left on the turntable for about 2 hr so that a state of equilibrium could be established in the moisture content of the test specimen and the rate of transmission of moisture could become uniform. The assemblies were then weighed, using a balance having a capacity of 1000 g and a sensitivity of 1 mg. The loss in weight over a period of 16 or 17 hr (overnight) was then recorded for each dish.

The influence of variations in the atmosphere may be effectively eliminated by the use of control dishes. Because of the cycling and the gradients of temperature and humidity to be expected in any controlled humidity room, it is considered necessary to define for each experimental run the straight-line relationship between the inverse of the rate of loss of moisture and the thickness of the air layer inside the dish. For each test, therefore, three control dishes were assembled with differing air-layer thicknesses inside the dish but without including a test specimen. The remaining dishes were assembled to include specimens to be evaluated. To avoid any troubles from convection, no air layer inside a dish was permitted to exceed 2 cm in thickness.

It will be understood that the resistance that is measured is the increase in resistance which results from the introduction of a test specimen into an assembly over that of a similar assembly which excludes the test specimen. If a rigid, incompressible material is being tested, its presence in the test equipment increases the distance between the water surface and the Orlon cover fabric by an amount equal to its thickness, and the total thickness of the air layers is equal to that in a similar assembly with no test specimen introduced. The difference in the resistances of these two assemblies is equal to the resistance of the test specimen. In the case of compressible materials such as fabrics, the increased distance between the water surface and the cover fabric when the sample is mounted in position in the testing equipment may not correspond to the thickness of the sample in a free, uncompressed state. This is due to the pressure applied at the perimeter of the test specimen in mounting, and the effect will be to reduce the thickness of the air layers above and below the sample. Account must be taken of this difference between the true and mounted thickness, and a correction must be made to the experimentally determined resistance in order to obtain the true value. This will be discussed further in connection with the experimental work on fabrics.

For materials having high resistances, e.g., equivalent to a 50 cm thickness of air or more, it is convenient and sufficient to use a medium-resistance lamina as a standard, and to assemble dishes containing the standard and unknown test specimen in an identical manner. If the rates of evaporation from the standard and the unknown assemblies are U_1 and U_2, respectively, the relation

$$\frac{U_1}{U_2} = \frac{R_L + R_x + R_e}{R_L + R_s + R_e} \tag{5}$$

may be employed, where R_L is the resistance of the air inside the dish, R_s the standard, R_x the unknown test material, and R_e the resistance of the external air layer. For very high-resistance materials a sufficiently accurate result can be obtained by a direct comparison of the inverse of the rates for a high-resistance standard and the unknown test specimen, since the experimental R_L and R_e may then be neglected in comparison with R_x and R_s.

Verification of Method by Measurement of the Diffusion Coefficient of Water Vapor in Air

The method described to determine the resistance to water-vapor diffusion of laminae in terms of equivalent air thicknesses can also be readily applied to determine the diffusion coefficient of water vapor in air. As this diffusion coefficient has been carefully studied by other methods, a valuable check on the procedure is provided.

Referring to equation (1), let p_a be the vapor pressure of the liquid in the dish and p_b be the vapor pressure in the room. It is seen that by changing the liquid p_a may be changed to p_a'. R may then be changed to R' such that the other quantities in the equation remain constant. If this is done for two dishes run simultaneously, we have for one:

$$R = (DAt/Q)(p_a - p_b) \tag{6}$$

and for the other

$$R' = (DAt/Q)(p_a' - p_b) \tag{7}$$

Subtracting,

$$R - R' = (DAt/Q)(p_a - p_a') \tag{8}$$

from which D can be evaluated if the difference $R - R'$ is a known change in the thickness of a layer of air within the dish, since all the other factors are known. In this way the vapor pressure of

the room, which is not subject to precise control or measurement, is eliminated. A convenient experimental arrangement is to determine the relationship between $1/Q$ and L, the thickness of the air layer inside the dish, for two series of dishes run simultaneously. In one series the vapor pressure of the liquid is p_a, in the other p_a'. The values of L in the individual dishes in each series are adjusted to cover the desired range. By plotting the relationships for the two series, D can be obtained from values of L corresponding to the same rate of moisture loss. Different values of p_a' were obtained by using sulfuric acid solutions of two different concentrations giving relative humidities of 85.7% and 91.6% and a saturated solution of potassium chromate giving 88% R.H., while p_a was given by pure water. The three values obtained are shown below.

Experiment	D (Calculated from Expt.)
1. Sulfuric acid solution	0.245 cm² sec⁻¹
2. Sulfuric acid solution	0.243 cm² sec⁻¹
3. Potassium chromate solution	0.246 cm² sec⁻¹

These experiments were carried out at temperatures between 20°C and 21°C. Since the partial pressure of water vapor in the air of the room does not enter into the calculation, the biggest error in the experiment lies in obtaining an accurate value of the air temperature. Accurate temperature measurement and control is necessary because of the dependence of the vapor pressure of the liquids in the dishes on this factor; this difficulty is not encountered in other experiments employed to find the resistance of a sample since room temperature is not involved in the calculations. The values for D given by the International Critical Tables for temperatures 20°C and 21°C are 0.249 and 0.250 cm² sec⁻¹, respectively. Therefore, the method being used for measuring the resistance of materials is considered to be capable of providing results of reasonable accuracy.

Conversion Factors

Results on the moisture impedance of laminae can readily be converted into moisture-transmission values with the help of the diffusion coefficient of water vapor in air. The diffusion coefficient is generally expressed in cm² sec⁻¹ units and is equivalent to the mass of water vapor in grams transmitted through 1 sq cm cross-sectional area per sec when the vapor-pressure difference is equal to a concentration difference of 1 g per cc at two points 1 cm apart. The variation of the diffusion coefficient with temperature and barometric pressure is given by

$$D = D_0(T/T_0)^{1.75}(p_0/p) \qquad (9)$$

where D_0 = the diffusion coefficient at 0°C and 760 mm Hg pressure (0.220 cm² sec⁻¹); T = the absolute temperature ($T_0 = 273$°K); p = the atmospheric pressure ($p_0 = 760$ mm Hg).

Probably the simplest conversion of equivalent air thickness to transmission values convenient for physiological interpretation can be made by use of a factor which expresses the water vapor in grams transmitted per square meter per hour under a vapor-pressure difference per centimeter of air equal to 1 mm of Hg. Division of this factor by the equivalent air thickness of the material will then give a mass of water vapor in grams which will be transmitted per square meter per hour for a vapor-pressure difference equal to 1 mm of Hg between the two surfaces under consideration. The factors to be used for the transformation are given below for four temperatures.

Temperature	Factor (F)
0°C	8.05
20°C	8.75
25°C	8.85
30°C	8.97

The amount of water vapor passed through the material is given in grams per square meter per hour per millimeter of Hg by $W = F/R$, where R is the equivalent thickness of still air of the material expressed in centimeters. In the case of clothing assemblies where the equivalent air thickness had been estimated for the various layers of fabric and air, the relevant vapor-pressure difference would be that between the surface of the skin and the external atmosphere.

The External Associated Air Layer and the Effect of Wind Velocity

When water vapor is transmitted through a lamina to a region of lower vapor pressure, a layer of air exists in which there is a vapor pressure gradient extending outward some distance from the surface of the lamina. The resistance of this layer as well as its dependence on ambient air velocity is of considerable interest. Though its thickness may vary from one instant to another owing to factors such as convection and turbulence, it is found to offer a

reproducible average resistance to the diffusion of water vapor when the measurement extends over a period of time.

Although a straight-line relationship is found to exist between the inverse of the rate of loss of moisture and the thickness of the air layer inside the dish, this is not in itself proof that the magnitude of the external associated air layer does not vary with change in the vapor-pressure gradient. If, however, the resistance of the external air layer does not vary with change in vapor-pressure gradient, the slope of the straight-line relation $1/U$ to L must be determined solely by the diffusion coefficient D and the vapor-pressure difference between the surface of the water in the dish and that of the surrounding air. To determine whether this is the case, control and measurement of the water vapor pressure in the surrounding air must be carried out with a fairly high degree of precision, closer than is necessary in the measurement of the resistance of an unknown material where a comparison of resistances is involved as in the method which has been described. The results of a typical experiment in which the thickness of the air layer inside the dish was varied are shown in Table I, the rate being quoted in milligrams per second for the total area of the dish. The operating temperature and relative humidity in the room were 20.2°C and 69.5%, respectively, giving a water-vapor pressure equal to 12.34 mm of Hg. The vapor-pressure difference between the water surface and the surrounding air was equal to 5.32 mm of Hg.

The value of the slope of this experimentally determined relation and that calculated on the assumption that it is determined only by the diffusion coefficient and the vapor-pressure difference between the water surface and the surrounding air are given below under Experiment 1. The comparison of experimental and calculated values for a second determination in which the vapor-pressure difference was equal to 5.88 mm of Hg is shown under Experiment 2.

	Slope (experimental)	Slope (calculated)
Expt. 1 $p_1 - p_2 = 5.32$ mm Hg	13.9	14.1
Expt. 2 $p_1 - p_2 = 5.88$ mm Hg	12.7	12.8

Calculation based on the average difference in slopes for the two experiments shows that as L varies from 0.5 to 2.0 cm the corresponding variation in R_e [see equation (3)] can be no more than about 2½%. It is therefore concluded that the vapor-pressure gradient has no important influence on the magnitude of the resistance of the external air layer associated with a fabric.

TABLE I

L (cm)	$1/U$ (sec/mg)
0.5	17.5
0.8	21.5
1.1	26.1
1.4	30.3
1.7	34.1
2.0	38.5

TABLE II

Wind Velocity (mph)	Thickness of Associated Layer (mm)
0.2	7.0
3.7	4.1
6	2.9
9	2.2
12	1.7

The effect of wind velocity. The thickness of the associated external air layer can be readily determined by measuring the rates of loss of moisture from dishes containing liquids or solutions having different aqueous vapor pressures but with equal air spaces and identical cover fabrics employed in the assemblies. The appropriate equation to consider is

$$U_1 - U_2 = \frac{D(p_1 - p_2)}{L + R_m + R_e} \qquad (10)$$

where U_1 and U_2 are the rates of loss of moisture through a fabric when the aqueous vapor pressures of the liquids used in two dishes are p_1 and p_2, respectively, L and R_m remaining constant. From this equation, knowing the values for the other terms, R_e can be determined. Experiments run simultaneously avoid the necessity of knowing the precise value of the vapor pressure of the external air, but reasonably accurate control and knowledge of the temperature is required because of the dependence of p_1 and p_2 and, to a lesser extent, of the diffusion coefficient D on this quantity.

The effect of wind velocity on the resistance of the associated air layer, R_e, was studied using the above method. Experiments were carried out in the relatively still air of the room and also in a wind tunnel with the air passing in a direction parallel to the surface of the fabric. To avoid disturbance of the

air flow, the tops of the dishes were made flush with a platform forming the base of the tunnel. The results, giving the values for R_e in terms of an equivalent thickness of still air, obtained at a series of different wind velocities are shown in Table II.

As a check on these values an alternative experimental procedure was followed. A series of experiments giving the relationship between $1/U$ and L was carried out under relatively still air conditions, and the best value for the slope (K) was calculated. The total resistance is given by $1/U = K(L + R_m + R_e)$, from which, R_m having been previously determined, the value of R_e can be found. A parallel experiment run in a wind tunnel provided a value for the total resistance under this condition of higher wind velocity. The difference between the two values of the total resistance at low and high wind speeds for the same value of L measures the decrease in R_e for the increase in wind velocity. Good agreement with the results cited above was obtained.

The importance of the external associated air layer will readily be recognized from the fact that in relatively still air conditions it is larger in magnitude than the equivalent thickness of still air of the majority of fabrics themselves. It therefore constitutes an appreciable portion of the total resistance of a clothing assembly to the passage of water vapor.

Part II: A Study of the Transmission of Water Vapor by Diffusion through Perforated Metal Plates

Abstract

The resistance to diffusion of a large number of perforated metal plates has been studied. Thickness, hole diameter, and number of holes per unit area were varied, and experimental relationships found between these variables. These empirical relations are used to derive the general expression:

$$R = \frac{T}{\beta} + 0.71d\left(\frac{1}{\beta} - \frac{1}{\sqrt{\beta}}\right)$$

for the resistance of a plate, where T = thickness of plate; d = diameter of each perforation; β = percentage area of perforation. It is shown that this expression is in agreement with one derived from theoretical considerations.

Introduction

The development of new or improved materials in which the property of water-vapor transmission is a prime consideration demands both an understanding of the different factors which can influence diffusion and a quantitative measure of their importance. Earlier work on the diffusion of water vapor through fabrics had not included a study of this kind, and an investigation was undertaken in an effort to extend present knowledge.

If textile materials particularly are kept in view and if the type of nonhomogeneity associated with them is considered, certain variables which can be expected to influence water-vapor diffusion immediately present themselves for study. The most important of these variables associated with the material itself are thickness of material through which diffusion must take place, the particular distribution pattern of the substances composing it, and the diffusion coefficients of these component substances. Considering textile fabrics more specifically, the distribution pattern may be thought of in terms of the size of holes or air spaces in the material and the frequency of their occurrence. The diffusion coefficients involved will be those of water vapor in air and in the particular type of fiber from which the fabric is made. It is recognized that other variables are also likely to be involved, such as the particular cross-sectional shape of a hole and variations in size and shape along its length, the path which it follows from one surface of the material to the other, and an assemblage of different types of holes or an irregular distribution of them in the one material. Clearly, however, any initial experimental investigation of the influence of variables in a material can most satis-

factorily be undertaken if the number of such variables is held to a minimum and chosen from those believed to be of primary importance.

Textile fabrics are in general complicated structures which do not lend themselves readily to precise geometrical definition. For these materials even the statement of such an elementary property as thickness cannot be made in a simple and unequivocal expression. Controlled and accurately known variation of many major factors, other than fiber composition, is not possible in a textile material. For this reason, attention was first turned to a study of perforated metal plates. Such plates can be prepared in a large range of thickness, and the size and number of holes in a given area can be varied between wide limits according to a definite experimental plan. Each of these three chosen variables, thickness, hole size (or diameter in the case of circular holes), and number of holes per unit area, is capable of measurement to a high degree of accuracy. It is further known that passage of moisture through a perforated metal plate is limited to the actual holes, thereby eliminating a further complicating factor which arises in fabrics and which can more simply be investigated separately. Accordingly an investigation was made of the resistance to transmission of water vapor through perforated metal plates in which the perforations consisted of circular holes, uniformly spaced, and passing through the plate at right angles to its surface. In addition to the experimental investigation, the transmission of water vapor through a simplified regular structure of this type was also considered from a theoretical standpoint.

Experimental

The method used to measure the resistance to passage of water vapor of perforated metal plates was that outlined in Part I. The plates were made in the form of brass discs with a diameter equal to the outside diameter of the test dishes. The useful area of the discs corresponded to a diameter of 8.29 cm, equal to the inside diameter of the test dishes. A range of 72 plates was constructed in which the number of holes, hole diameter, and thickness of plate were varied to provide information on the effect of each of these three variables on plate resistance. The holes were grouped in a regular array such that the useful area of a plate might be imagined as divided into a number of equal contiguous hexagons with a hole at the center of each. Since at the circular edge of the useful area the hexagons do not coincide with the circle, precautions were taken to minimize edge effects. For the number of holes in a plate only certain values were chosen which gave minimum area defect and excess at the edge when the hole spacing was adjusted to make overall shortage and surplus equal. Great care was exercised in the drilling of the holes so that they would be as uniform and accurate as possible. This latter entailed an initial drilling of each hole with a drill one size smaller than that required, followed by a second drilling using a drill of the desired final size. Any slight burrs were carefully removed. A final check on each plate was made through microscopic measurement of the diameter of a number of holes taken on each side of the plate; the average deviation of these readings for each plate was in all cases found to be less than 1%. The mean value obtained for each hole diameter is that recorded in the presentation of results. The two plates with the largest number of holes, 1980 and 5450, were cut from commercially perforated brass sheet and the holes enlarged slightly by drilling to make them uniform and cylindrical.

After inserting the plate between the top of the brass dish and the bottom of the upper ring of the experimental apparatus, a seal was provided by the

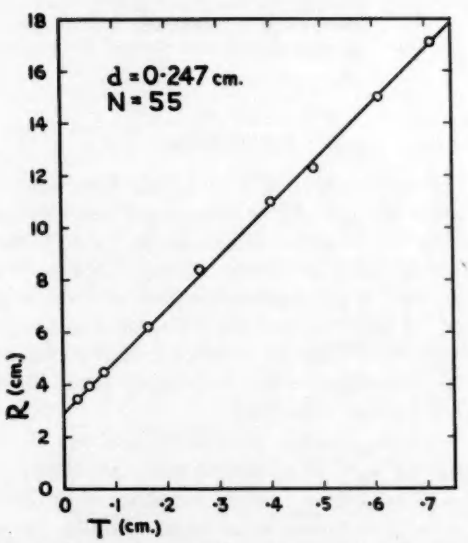

Fig. 3. Typical relationship between the resistance to diffusion of water vapor and the thickness of perforated plates of the same pattern. The intercept on the R axis represents the resistance of an infinitely thin plate.

TABLE III

d	N	D^2/Nd^2	a_1
0.247	421	2.68	2.70
0.247	55	20.5	20.0
0.0905	421	20.0	20.7
0.0905	55	152	146

use of electrician's rubber tape, as previously described. This was not found to be absolutely perfect; the possibility existed of leakage up to 5 mg over a 16-hr period where a relatively impermeable material was being tested, but the resulting error was serious only in plates having a resistance greater than 50-cm thickness of still air. The possible error arising in these cases could be reduced by a slight modification of the experimental procedure and the method of calculation employed.

A complete table of results on all 72 plates is given in Appendix I. For convenience in interpretation and discussion, selected series from the total range of plates are here presented, in which two of the three chosen variables are held constant.

The following notation is used: $T =$ thickness of plate in centimeters; $d =$ diameter of hole in centimeters; $N =$ number of holes in the total area of the plate (54.0 cm^2); $R =$ resistance of plate in centimeters of still air.

1. T *variable,* d *and* N *constant.* The relationship between R and T, with d and N constant, is illustrated in Figure 3. These particular results are for the most extended series of thickness values examined, and may be taken as typical of all results obtained from examining the relationship between resistance and thickness. The experimental relationship when d and N are constant may be written:

$$R = a_1T + b_1 \tag{11}$$

where b_1 is the intercept on the resistance axis. The value of b_1 may be regarded as the resistance offered by an infinitely thin plate of the pattern under consideration. It is the resistance which results from the plate preventing uniform vapor flow at all points in its surface. The actual flow lines will in fact converge from a plane of uniform vapor pressure at some distance from the plate to the holes through which the water vapor must pass. Similarly, there will be divergent lines of flow from the holes on the side of lower vapor pressure.

The slope of the line a_1 in equation (11) agrees within experimental error with the ratio of the total area of the plate to the perforated area. This ratio is given by D^2/Nd^2, where D is the useful diameter of the plate. Computed values for four series embracing widely different values of d and N and the corresponding values of a_1 are given in Table III.

TABLE IV. $T = 0.0508$ cm

	R (cm of still air)				
N	$d=0.0583$ cm	$d=0.0905$ cm	$d=0.158$ cm	$d=0.247$ cm	$d=0.410$ cm
7	312	141	59	36.0	17.5
19	97	50	22.0	12.7	5.90
55	35.2	18.0	7.74	3.96	1.73
151	12.3	6.20	2.48	1.20	0.40
421	4.29	2.04	0.76	0.29	
1123	—	0.72	0.24		
1980	0.76				
5450	0.27				

TABLE V. $T = 0.165$ cm

	R (cm of still air)			
N	$d=0.0905$ cm	$d=0.158$ cm	$d=0.247$ cm	$d=0.410$ cm
7	299	79	46	24.8
19	101	36.4	19.0	8.75
55	34.1	12.5	6.21	2.57
151	12.1	4.43	2.02	0.71
421	4.46	1.45	0.59	
1123	1.55	0.51		

The resistance of a plate may therefore be expressed by the relation

$$R = \frac{D^2}{Nd^2}T + b_1 \tag{12}$$

where b_1 has some value dependent upon the number and size of holes but not upon their depth.

2. N *variable,* T *and* d *constant.* Tables IV and V show results for nine series of plates in each of which series N is allowed to vary while T and d are held constant.

When the resistance R is plotted against $1/N$, T and d being constant, a straight line provides a reasonably good fit to the experimental points. There is, however, an indication of curvature, and that such a curvature in the relation $R = a/N$ does exist can be seen by including a point in which N approaches its limiting value of D^2/d^2.[3] In this case the re-

[3] This value could not be reached with round holes, since at $N = 0.907D^2/d^2$ neighboring holes would become tangent. However, it can be seen that, as the proportion of area perforated approaches totality, the distortion of the flow pattern by the plate approaches zero and hence the shape of the holes becomes unimportant. It is therefore permissible to allow the hole shape to approach hexagonal as N approaches D^2/d^2.

sistance must approach a value equal to T cm, the thickness of the plate. A straight line fitted to the experimental values cannot be made to include this point. A good fit to all points, including the latter, is found in the relation

$$R = A_2/N + B_2/\sqrt{N} \qquad (13)$$

where A_2 and B_2 are constants. A typical set of results in which $T = 0.0508$ cm and $d = 0.0905$ cm is shown in Figure 4, including the limiting case where $N = 8390$ and $R = 0.0508$ cm. Agreement with the relation $R = A_2/N + B_2/\sqrt{N}$ is to be seen in the linear fit of the points obtained by plotting $R\sqrt{N}$ against $1/\sqrt{N}$. Similar graphs were drawn for ten series of plates and used in a further manner to be described in section 4 below.

3. d *variable,* T *and* N *constant.* All graphs of R against d and d^2 or their inverses show marked curvature; no function of d was found to be linear with R when T and N were held constant.

4. N *and* d *variable,* Nd^2 *and* T *constant.* Consideration of a series of plates in which both N and d vary while the total perforated area given by $\pi Nd^2/4$ remains constant leads to more fruitful results than where d only is allowed to vary. This case has particular interest also in that it would indicate whether, where a high vapor permeability is required in a structure having a fixed percentage of its surface area permeable, there is an advantage to be gained by having that permeable area in the form of a large number of small holes, or a lesser number of larger holes.

The actual preparation of a series of perforated plates in which the perforated area is kept constant, although envisaged in the original planning, was found to be too difficult and inconvenient to attain with any high degree of accuracy. Selection from available drill sizes combined with choice of number of holes could, however, be made to provide a series of plates in which the perforated area remained approximately the same, and certain such series are contained in the data given in the table in Appendix I. Correction would have to be applied, of course, for such deviations from constancy as do exist, and the method by which to correct is uncertain. A more satisfactory procedure can be based upon data from the graphs of section 2 above. For any chosen value of perforated area, the values of N and R can be found corresponding to a series of values of d.

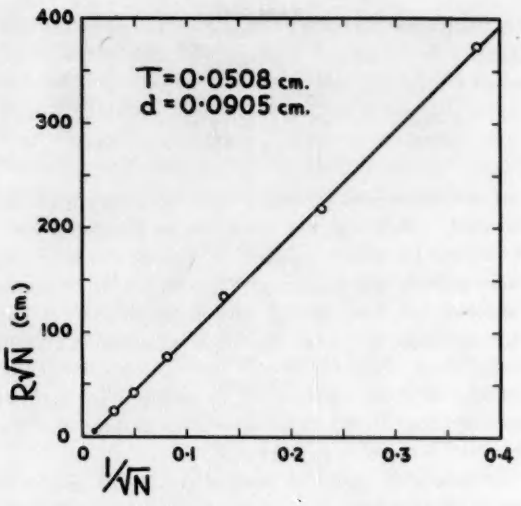

Fig. 4. A relationship of the form $R = A_2/N + B_2/\sqrt{N}$, where N is the number of holes, fits all experimental values for plates of the same thickness and hole diameter, including the theoretical limiting case in which the perforated area reaches 100%.

In Table VI is given a set of readings corresponding to perforated areas equal to 0.1%, 1%, 5%, 10%, and 40% of the total plate area, the thickness of the plate being 0.0508 cm in all cases.

For a constant perforated area, a linear relation exists between the resistance of the plate and the diameter of the holes. This is illustrated graphically in Figure 5 for the series given in Table VI in which the perforated area is equal to 5% of the total area of the plate. For the condition that Nd^2 and T are constant, the relation between resistance and hole diameter may therefore be written

$$R = a_3 d + b_3 \qquad (14)$$

where a_3 and b_3 are constants.

It will be clear that for a fixed perforated area the diameter of the holes has a marked influence on the resistance of the plate; to achieve low resistance it is a great advantage to have the perforated area in the form of a large number of fine holes rather than a fewer number of larger holes.

Discussion of Results

The linear relations found experimentally in sections 1 and 2 above may be written

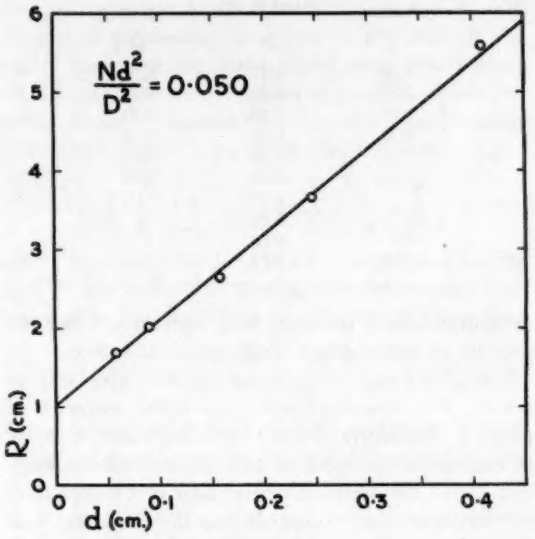

Fig. 5. For plates having the same percentage perforated area, the resistance to water-vapor diffusion increases linearly with the diameter of the perforations. Low resistances are achieved with large numbers of small holes rather than a smaller number of larger holes.

$$R = \frac{D^2}{Nd^2} T + b_1 \tag{15}$$

(d and N constant), and

$$R = \frac{a_2}{N/D^2} + \frac{b_2}{\sqrt{N/D^2}} \tag{16}$$

(T and d constant).

The form of the second equation is a slight modification of that originally given in section 2 by the introduction of the term D^2, which is proportional to the area with which N is associated. A corresponding change is, of course, involved in the values of the constants. The resistance R, expressed as the thickness of a layer of air of equivalent resistance, is a function of the thickness of the plate T, the diameter of the holes d, and the number of holes per unit area ($4N/\pi D^2$). Considering equation (15), where d and N are constant, the term b_1 can at most be a function of d and N/D^2, and may be written $f(d, N/D^2)$. In equation (16), a_2 can be a function of T and d only, say $\phi(T, d)$, and similarly b_2 can be a function of T and d only, $\psi(T, d)$. Equating the right-hand sides of these two equations, we have the identity

$$f\left(d, \frac{N}{D^2}\right) = \frac{D^2}{N}\left[\phi(T, d) - \frac{T}{d^2}\right] + \frac{D}{\sqrt{N}}\psi(T, d) \tag{17}$$

It follows that $[\phi(T, d) - (T/d^2)]$ and $\psi(T, d)$ must be functions of d only, and may be written as $\theta(d)$ and $\psi(d)$, respectively. Therefore

$$f\left(d, \frac{N}{D^2}\right) = \frac{D^2}{N}\theta(d) + \frac{D}{\sqrt{N}}\psi(d) \tag{18}$$

Since R has the single dimension of length, it is clear that $b_1 = f(d, N/D^2)$ must also have the single dimension of length. Therefore $\theta(d) = K_1/d$ and $\psi(d) = K_2$, where K_1 and K_2 are numerical constants. Hence

$$f\left(d, \frac{N}{D^2}\right) = K_1\frac{D^2}{Nd} + K_2\frac{D}{\sqrt{N}} \tag{19}$$

for $d = D$, $N = 1$. In this case R must equal T and b_1 must be zero. It follows that K_1 must be equal to $-K_2$, and therefore

$$b_1 = K_1\left(\frac{D^2}{Nd} - \frac{D}{\sqrt{N}}\right) = K_1 d\left(\frac{D^2}{Nd^2} - \frac{D}{\sqrt{N}\,d}\right) \tag{20}$$

The general equation for R may then be written

$$R = \frac{T}{\beta} + Kd\left(\frac{1}{\beta} - \frac{1}{\sqrt{\beta}}\right) \tag{21}$$

where β is the ratio of the open area to the total area Nd^2/D^2. It will be seen that the third relation

TABLE VI. T = 0.0508 cm

	% Perforated Area ($Nd^2/D^2 \times 100$)									
	0.1%		1.0%		5.0%		10.0%		40.0%	
d (cm)	N	R (cm)	N	R (cm)	N	R (cm)	N	R (cm)	N	R (cm)
0.0583	20.2	95	202	9.1	1.01×10^3	1.68	2.02×10^3	0.79	8.08×10^3	0.15
0.0905	8.41	115	84.1	10.9	420	2.02	841	0.95	3.36×10^3	0.18
0.158	2.75	150	27.5	14.4	137	2.65	275	1.24	1.10×10^3	0.24
0.247	1.13	215	11.3	20.4	56.2	3.66	113	1.67	450	0.28
0.410	0.41	337	4.09	31.6	20.4	5.59	40.9	2.49	164	0.38

found experimentally, namely $R = a_3 d + b_3$ when Nd^2 and T are constant, is in accord with the above equation. The good fit provided by this general equation to the experimental results is indicated by the stability in the value of K calculated from the results for each individual series of plates. The actual values for twenty series are shown in Table VII, in which those under A are obtained from the experimental values when T varies with d and N constant, those of group B are from the series in which N varies with d and T constant, and those of group D when d varies with Nd^2 and T constant.

The average value for K obtained from all the experimental results is 0.71, and the general empirical formula for the resistance of a plate may be written

$$R = \frac{T}{\beta} + 0.71d\left(\frac{1}{\beta} - \frac{1}{\sqrt{\beta}}\right) \qquad (22)$$

Theoretical Consideration of the Resistance of Perforated Plates

Consider a cylinder of air of circular cross section equal to the area of a perforated plate. Let one of the flat end faces of the cylinder be a source of water vapor at a fixed pressure, and the other end a sink at some lower vapor pressure, the curved walls of the cylinder being impervious. With the object of arriving at a theoretical expression for its resistance, imagine a plate placed midway between the end faces of the cylinder and consider the movement of the water vapor by diffusion through the cylinder.

In the absence of convection, and if the cylinder is of sufficient length, the water-vapor isobaric surfaces will be plane near the cylinder ends, but will become increasingly dimpled as the plate is approached. This is because the lines of flow, which are parallel and uniformly spaced near the ends, must be made to converge into the holes. The pattern of flow lines obviously must be symmetrical about the central plane of the plate. Again, from symmetry, it is clear that (neglecting plate-edge effects) the flow lines passing through any one hole expand on either side of the plate to fill a hexagonal cylinder, and that all such cylinders fit together to fill up the entire space.

The resistance from one end face to the other is a function only of the length of the cylinder and of the geometry of the plate. The differential equation and boundary conditions governing the flow of water vapor can be set up in a straightforward manner. However, the exact solution is beset by mathematical difficulties which have not been overcome. For the present an approximate treatment must suffice.

TABLE VII

A	*B*	*D*
0.80	0.77	0.70
0.72	0.81	0.72
0.75	0.78	0.71
0.57	0.68	0.71
	0.69	0.70
	0.60	0.67
	0.77	
	0.62	
	0.70	
	0.74	

Let C = length of cylinder of still air; and as before, T = plate thickness; D = useful diameter of plate; d = diameter of holes; R = resistance in terms of equivalent thickness of still air, defined by equation (1). The simplest type of flow in a region having constant cross section is one in which the flow lines are parallel to the walls and uniformly distributed over the cross section. The resistance of the holes in the plate in this case would be:

$$T\,\frac{\pi D^2/4}{N\pi d^2/4} = \frac{TD^2}{Nd^2} \qquad (23)$$

and the resistance of the remaining space would be $(C - T)$. Taken together these would give a total resistance from one end face of the cylinder to the other, equal to

$$C - T + (TD^2/Nd^2) \qquad (24)$$

This, however, neglects the obvious necessity of joining the flow lines at the two surfaces of the plate. To do so would require regions of converging and diverging flow which would entail a corresponding increase in the total resistance, because the flow coming out of a hole, for instance, cannot immediately expand its cross section to that of the hexagonal cylinder.

As an approximation for this increase let us take the resistance of a flow which expands in cross section [4] as rapidly as possible from that of the hole to that of the corresponding hexagonal cylinder. Put another way, the assumption is being made that joining the flow lines involves an increase equal to the minimum possible resistance for flow of any configuration between isobaric surfaces having the two areas in question. The greater the curvature of

[4] The cross section of a flow is the area of the isobaric surface at the point in question.

these surfaces the lower is the resistance encountered by a flow proceeding from one to the other. The maximum curvature which could exist just outside a hole in a plane barrier would be given by concentric hemispheres. The resistance in this case is easily calculable. For N holes in parallel it becomes

$$\frac{1}{N}\left(\frac{\pi D^2}{4}\right)\int_{r_1}^{r_2}\frac{dr}{2\pi r^2} = \frac{D^2}{8N}\left[\frac{1}{r_1}-\frac{1}{r_2}\right] \qquad (25)$$

where r_1 is given by $2\pi r_1^2 = \pi d^2/4$ and r_2 is given by $2\pi r_2^2 = \pi D^2/4N$. Substituting these values and multiplying by 2 to include both sides of the plate gives

$$\frac{1}{\sqrt{2}}\left[\frac{D^2}{Nd}-\frac{D}{\sqrt{N}}\right] \qquad (26)$$

The total resistance from one end face of the cylinder to the other will now be the sum of equations (24) and (26). To get the resistance of the plate it is necessary to subtract the thickness $(C - T)$ of all air layers external to the plate. If, in addition, β is written for the perforated fraction of the plate area (i.e., $\beta = Nd^2/D^2$), the expression for the resistance of the plate takes the form:

$$R = \frac{T}{\beta} + \frac{d}{\sqrt{2}}\left(\frac{1}{\beta}-\frac{1}{\sqrt{\beta}}\right) \qquad (27)$$

It will be seen that this relation is identical in form to the empirical equation derived from the experimental data. Moreover, the value 0.71 found for K from the experimental results agrees with the value $1/\sqrt{2}$ in the equation just derived. The coincidence of these two values is somewhat surprising and demonstrates that the assumption made above is substantially correct.

Part III: The Resistance of Fabrics to the Passage of Water Vapor by Diffusion

Abstract

The water-vapor diffusion resistances of textile fabrics covering a wide range of weights, constructions, and fiber types have been measured. An overall linear but non-proportional relationship between resistance and thickness is apparent. The influence of percentage fiber volume and fiber distribution in the fabric is indicated. An empirical formula expressing resistance in terms of thickness and fiber volume is shown to describe reasonably well the behavior of most woven fabrics. Materials exhibiting considerable deviation were found to possess either very high or very low air permeability. A variety of evidence, including measurements of the resistance of films, leads to the conclusion that, with the possible exception of the densest fabrics under conditions of very high humidity, transmission of water vapor by the fiber does not contribute appreciably to the diffusion resistance of the fabric as a whole.

Introduction and Experimental Procedure

In a study of the factors which contribute to the resistance offered by fabrics to the diffusion of water vapor, a wide range of textile materials was selected for examination. This comprised fabrics made from wool, cotton, viscose rayon, acetate, nylon, Orlon, Saran, polyethylene and Fiberglass, and included a variety of weights and weaves. The range was made to cover fabrics from sheer, open structures made from fine filament yarns to thick wool felts. In addition, certain materials in the form of films such as cellophane, nylon, and polyethylene film were measured both for their intrinsic interest and to assist in elucidating the part played by the fiber in the transmission of water vapor through a fabric. In this latter connection also, a special series of fabrics was woven from different fibers to as near identical yarn and cloth structure as was practically feasible.

All the factors which are fundamentally important in determining the resistance of a fabric to water-vapor diffusion may not of themselves be readily measurable. In this case other properties which might be correlated with these factors, and which are more easily measured, may be sought. For this reason, in addition to the measurement of resistance to diffusion, the structure of each fabric was analyzed,

its thickness, weight, and bulk density were determined, and its air permeability was measured.

The measurement of fabric thickness presented the greatest problem. Two important differences from a rigid solid lamina are to be recognized. In the first place, fabrics in general are readily compressible; in the second place their surfaces are not well defined. An instrument for measuring fabric thickness customarily places the material between two plane parallel plates under some chosen pressure and the distance separating the plates is read off as the thickness. The result, however, may lie anywhere in a considerable range, depending on the pressure selected. In other words, the thickness of a fabric determined by direct experimental techniques may be unduly influenced by a few resistant fibers, or may represent the fabric in a state of compression unrelated to its normal configuration, depending upon whether the pressure applied is low or high. Certain studies have been made elsewhere in an attempt to find a relationship between measured thickness and pressure which would permit extrapolation to pressures below the range in which satisfactory and reproducible measurements may be made. By such methods it might be possible to arrive at a value of thickness at zero pressure. It is true that the vapor-transmission measurements are made with fabrics in an uncompressed state, but thickness values obtained by extrapolation to zero pressure may be inapplicable because of a further difficulty. Unlike a solid lamina, a fabric has no clearly distinguishable surfaces which define its boundaries and permit an unequivocal statement of thickness. This is illustrated particularly well in a fabric having a small proportion of fibers projecting a relatively large distance outward from the body of the cloth. It is possible for the thickness of this fabric, as determined under a pressure which approaches zero, to be greatly influenced by these projecting fibers although their contribution to vapor resistance may be practically nil. Thickness measured by methods customarily employed cannot be regarded as the most satisfactory value with which a particular fabric property might be related.

At the present time no solution is seen to the problem of the definition of fabric thickness. It is believed that the thickness most appropriate to the present resistance studies will be less than that embraced by the extreme limits to which fibers extend outward from the center of a cloth, but there is no means of knowing a priori what the appropriate pressure to apply would be. Having regard for correlation with any particular fabric property, it is unlikely that to obtain comparable thickness values, the pressure to be applied in measurement will be the same for all fabrics. In the absence of anything known to be better, an arbitrary but low pressure has been adopted in determining the thickness of fabrics studied in this report. In all cases thickness values stated are those corresponding to a pressure of 0.05 psi, measured between flat plates covering an area of approximately 10 sq in.

The measurements of resistance to transmission of water vapor were carried out using the experimental equipment and procedure essentially as described in Part I. The method employed involves measuring the total resistance of two layers of air plus the test specimen and subtracting from this the resistance of the air layers. The thickness of the air layers must therefore be known accurately. With an incompressible plane lamina as a test specimen this presents no particular difficulty. If, however, the test sample is compressed at its perimeter where mounted, the compressed thickness will be less than the thickness of the specimen in the free state, and therefore less than the thickness of that portion of the mounted sample through which the diffusion is taking place. The net result is to reduce the total thickness of the air layers by an amount equal to the difference between the uncompressed and compressed values of thickness of the sample. Although in most cases this difference will not be large, it must be taken into account as a correction. In practice it is necessary only to calculate the thickness of the test specimen at its perimeter as mounted (the distance between the upper edge of the brass dish and the lower edge of the brass ring, as shown in Figure 2) and find by how much this is less than the value taken to be its thickness in the uncompressed state. The difficulty of measuring the "effective" thickness of a fabric has already been discussed, and thickness in the uncompressed state is here taken arbitrarily as that measured under a pressure of 0.05 psi. This almost certainly introduces an error, but one which, as a percentage of the total resistance, is likely to be small in most cases. This will be recognized more clearly from an examination of the experimental data.

For certain few materials some modification in the method of mounting was necessary. In the case of thick felts, samples were cut to a size equal to the external diameter of the test dish and an adequate seal was applied to prevent loss of vapor laterally

TABLE VIII

Identification	Resistance R (mm of air)	Thickness T (mm at $p=0.05$ psi)	% Fiber Volume V_f ($p=0.05$ psi)
1. Cotton, plain	1.3	0.31	32
2. Cotton, twill	1.5	0.41	24
3. Cotton, chambray	1.5	0.51	24
4. Cotton, drill	2.2	0.60	31
5. Cotton, drill	1.9	0.69	27
6. Cotton, drill	2.2	0.81	24
7. Cotton, drill	2.5	0.94	24
8. Cotton, oxford	1.8	0.53	28
9. Cotton, duck	2.7	0.83	27
10. Cotton, duck	2.5	0.91	20
11. Cotton, duck	3.1	0.94	24
12. Cotton, duck	3.1	0.95	29
13. Cotton, duck	3.4	1.19	29
14. Cotton, ticking	2.4	0.94	21
15. Cotton, flannelette	1.9	0.99	10
16. Cotton, canvas	2.5	0.97	29
17. Cotton, plain knit	1.2	0.84	14
18. Cotton, warp knit	0.7	0.81	12
19. Cotton/viscose and hair, plain	2.8	1.17	16
20. Cotton/wool, plain knit	1.3	1.19	10
21. Wool, serge	2.9	1.05	27
22. Wool, twill	2.9	1.35	19
23. Wool, melton	6.0	2.3	24
24. Silk, crepe	0.8	0.15	28
25. Acetate, sateen	1.3	0.13	53
26. Viscose/acetate, plain	1.1	0.25	35
27. Viscose, plain	0.9	0.19	34
28. Viscose, twill	1.5	0.19	43
29. Viscose, plain	1.3	0.43	19
30. Viscose, plain	2.1	0.57	28
31. Viscose (Tenasco), matt	4.9	0.84	52
32. Viscose/cotton, sateen	1.5	0.44	26
33. Nylon, plain	0.7	0.13	35
34. Nylon, plain	1.9	0.16	48
35. Nylon, plain	1.1	0.17	41
36. Nylon, marquisette	1.0	0.20	21
37. Nylon, sateen	1.2	0.25	37
38. Nylon, twill	1.8	0.3	46
39. Nylon, net	1.3	0.44	27
40. Nylon, twill	2.1	0.6	23
41. Orlon, plain	5.8	0.94	39
42. Saran, plain	1.4	0.97	19
43. Polyethylene, twill	2.8	0.75	45
44. Glass, plain	1.0	0.15	29
45. Glass, plain	3.0	0.22	40
46. Glass, twill	3.8	1.5	21
47. Felt	2.8	1.9	11
48. Felt	3.9	2.5	13
49. Felt	5.3	3.5	12
50. Felt	7.5	5.2	10
51. Felt	7.1	5.3	10
52. Felt	13.3	8.3	14
53. Felt	17.5	9.5	18
54. Felt	13.7	11.9	6
55. Felt	17.6	13.3	9
56. Felt	23.6	13.8	15
57. Felt	20.5	15.2	9

through the fabric edge. A similar procedure was adopted for leather samples.

Air permeability was measured at 65% R.H. and 70°F, using the Frazier Air Permeability Tester designed at the U.S. Bureau of Standards. The figures recorded give the air permeability in cubic feet of air per square foot per minute passing through the material under a pressure differential equal to 0.5 in. of water. Percentage fiber volume in a fabric was calculated from the fiber density and fabric density, thickness being measured as described above.

Results and Discussion

In Table VIII are shown the resistance to diffusion, thickness, and percentage fiber volume obtained on 57 samples of material. More detailed descriptions of the fabrics are found in Appendix II.

General Considerations

Consideration of factors involved in the total resistance of a fabric can be assisted by reference to the results on perforated metal plates previously discussed in Part II. In the case of such a plate it was shown that the total resistance comprises a term involving plate thickness and a second term governed by the number and size of the perforations. This latter resistance arises as a result of the interposition of a surface which is nonhomogeneous in its vapor-transmission characteristics, thereby disturbing the normally plane vapor-pressure isobars. Similarly, in any heterogeneous material, such as a fabric, it is clear that there must be resistance components similar in character to those associated with a plate, namely, an external resistance dependent upon the surface configuration and an internal resistance of which thickness of material is a factor. Important differences must immediately be recognized between perforated plates and fabrics, however, which preclude any direct application to textile materials of the resistance formula derived for plates. Within the limitations imposed by yarn and cloth structure, the fibers in a fabric form a jumbled mass in which, generally, direct air channels from one surface to the other do not exist. Variation in the percentage fiber volume V_f (the ratio of fiber volume to fabric volume) must therefore influence both the cross section and the length of path of air through which vapor must diffuse in passing from one surface of the fabric to the other. The coefficient of the thickness

term will consequently depend in some manner upon V_f, and will be greater than for a perforated metal plate with the same percentage solid volume. It has also been pointed out that because of the fibrous structure of a fabric the concept of thickness requires modification so far as vapor transmission is concerned, and represents something less than the distance between the extremes to which fibers extend out from the center of the cloth. Further differences between textile fabrics and regularly perforated metal plates lie in the actual air-to-solid ratio and in the size, distribution, and shape of the apertures or air channels. The large majority of textile structures have a fiber volume less than 50% of the total volume of the fabric, and in most cases very considerably less. In the preparation of perforated metal plates it was not found feasible to drill holes smaller than 0.58 mm in diameter nor to exceed a perforated area equal to 50% of the total plate surface. Fabrics, therefore, in addition to differences associated with the irregular path of an air channel, are considerably beyond the limits of air volume and fineness of hole covered by actual investigation on metallic plates, and extrapolation of the results on the latter into this region may be open to question.

In Figure 6 is shown resistance R plotted against measured thickness of material T for all fabrics tested. While a general upward trend in resistance is noted with increasing thickness, the experimental observations are rather widely scattered. It is fairly obvious, therefore, that, in agreement with the preceding discussion, variables other than thickness are involved which mask the possible existence of any simple linear relation between resistance and thickness.

Examination of the data for individual points in Figure 6 shows that, for fabrics of approximately equal thickness, resistance varies directly with percentage fiber volume V_f. This has already been anticipated, and in order to study further any relationship between thickness and resistance it is desirable to eliminate the influence of this variable. While this is not completely possible with the data available, a selection can be made of fabrics whose percentage fiber volumes fall within a restricted range. In Figure 7 are shown the values for resistance plotted against thickness for 23 fabrics having percentage fiber volumes in the range 20 to 29%, inclusive. This particular range was chosen on the basis of highest frequency of occurrence of

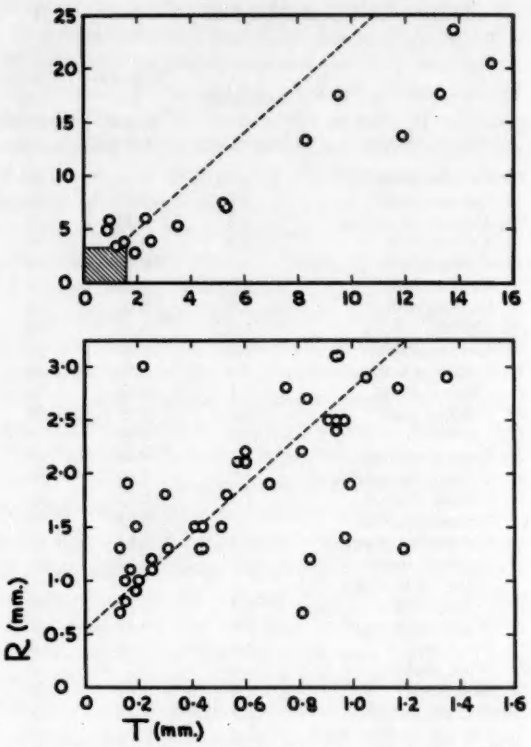

Fig. 6. Resistance of all fabrics tested plotted against their measured thickness. The straight line found in Figure 7 for fabrics having fiber volumes between 20% and 29% is shown for comparison.

fabrics in a 10% interval. It may be noted that none of these fabrics possessed an abnormally high or low air permeability, a point which will be referred to later. A reasonably good linear relationship between R and T is seen to exist in the results on these fabrics. The equation of the particular line drawn in Figure 7, calculated by the method of least squares, is $R = 2.25T + 0.55$, where R and T are expressed in millimeters. The actual values so obtained for the coefficient of T and the intercept on the resistance axis are not to be regarded as possessing a high degree of accuracy, and both must have a dependence on percentage fiber volume. It would be desirable to attempt experimental measurements on an adequate number of fabrics in several limited ranges of percentage fiber volume to secure information not available in the existing data.

It has been stated that in fabrics, as in the case of perforated metal plates, the total resistance must embody an external-resistance term independent of

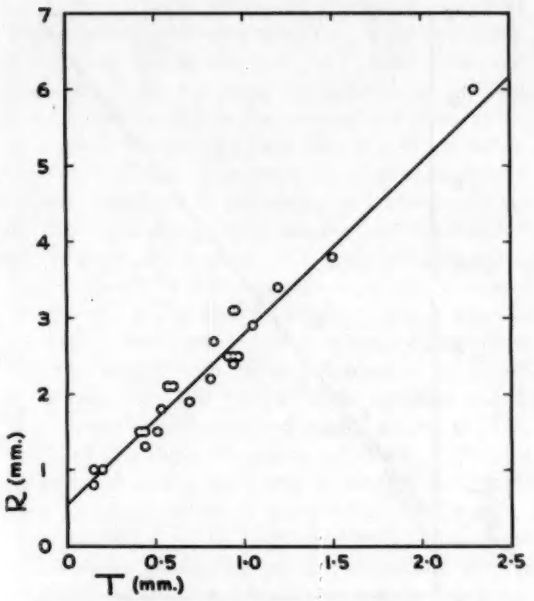

Fig. 7. The resistance of 23 fabrics having percentage fiber volumes in the range 20 to 29% shows a linear relationship with measured fabric thickness. Fabrics of abnormally high or low fiber volume deviate from this relation (cf. Figure 6).

thickness, and an internal-resistance term of which thickness is a factor. Further consideration of the resistance of a fabric can most profitably be pursued by the separate examination of these two components.

The External-Resistance Component

The surface of a fabric is clearly not comparable in physical configuration to the surface of a perforated metal plate of the type investigated. Although the effect on vapor transmission of the differences which exist cannot be readily assessed, certain points of divergence may be suggested and the direction of their influence indicated. The external-resistance component is conceived as arising when a diffusion flow undergoes a transition between two regions, one in which there is no obstruction, the other in which the flow cross section is restricted to a smaller but more or less constant value in the body of a porous solid. The first difference between plates and fabrics is that the change of cross section is abrupt in one case and gradual in the other. In general, the outermost layers of a fabric are not as dense as the central layers. Progressive restriction of the cross section

TABLE IX

Material	Resistance (mm) 1 Layer	2 Layers	3 Layers
Viscose rayon lining	1.8	3.0	4.3
Nylon marquisette	1.0	1.5	2.2
Wool serge	2.6	4.4	6.3
Glass fabric	1.6	2.6	3.7

of flow must occur such that the change begins at the outermost fibers, but only after some depth has been reached can an effectively constant value be established. It is also to be noted that a portion of the air spaces in a fabric will be "cul-de-sacs" so far as vapor flow is concerned. Both effects will tend in the same direction, resulting in a surface effectively less porous than that of a plate having the same percentage solid volume, and in a correspondingly higher external-resistance component. Lacking any principle by which the geometry of a fabric might be translated into some equivalent form of metal plate, the formula developed for the latter cannot be used to predict the external resistance of a fabric.

The existence of an external resistance and a measure of its magnitude in a material having a large number of very fine pores was, however, investigated in the following way. Two fritted glass discs about 4 mm thick having pore sizes in the range 10 to 20 μ were obtained and the faces ground sensibly smooth. From density calculations these discs were found to be 53% solid material and 47% air. The resistances of the two discs were measured when in direct contact and again when separated by a 3-mm spacer ring. The values obtained were 16.9 mm and 17.3 mm of air, respectively. The difference of 0.4 mm is to be attributed to a reduction in the number of free surfaces from 4 to 2, and therefore equal to the external resistance associated with 1 plate.

Fabrics present a more difficult problem to investigate in this way because of the greater uncertainty associated with the contact between one layer and another. Very light contact probably involves an air layer between the two specimens, while the application of deliberate pressure may cause an embedding of one into the other, thereby diminishing the effective thickness of the two. By choosing suitably smooth-surfaced materials, however, the probability of this latter is reduced, and poor contact would result in less difference between the first and additional layers than would otherwise be the case. The results in Table IX are therefore of some in-

terest, even though some uncertainty exists regarding their degree of accuracy.

The external resistance to be associated with the two surfaces is given by the difference between the resistance of one layer and the increase effected by the addition of each additional layer in contact with it. From the results given in Table IX, the values so calculated for the external resistances of the four fabrics will be seen to be 0.55, 0.40, 0.75, and 0.55 mm of air, values which agree satisfactorily with the magnitude of the intercept on the resistance axis shown in Figure 7. It is undoubtedly true, however, that this external-resistance term will vary from one fabric to another, although for the majority of fabrics the extent of the variation may not be large.

Certain important conclusions are to be drawn from a recognition of the fact that the total resistance of a fabric does not reside wholly in the passage of water vapor within the fabric itself. Any method which simply determines the increase in resistance due to the addition of a second layer in contact with the first, is likely to introduce error by partial or total elimination of the external-resistance term. In the case of very thin fabrics this external resistance may be as large as the internal resistance, or even larger. Comparison of the resistances of fabrics of different thickness based on a computed resistance per unit thickness, i.e., R/T (a method which was resorted to in some of the earlier work on vapor transmission), is clearly an inadmissible procedure, and likely to lead to wrong conclusions on the relative transmission properties of fabrics of different fiber composition. For example, a comparison of the resistance of a nylon fabric, which is usually thin, with a wool fabric, which is normally thick, would lead to the conclusion that nylon materials have a very much higher resistance per unit of thickness than materials composed of wool. Comparison of the resistances of different materials will be referred to again in more detail later.

The Internal-Resistance Component

Consider, now, that portion of the resistance which is dependent upon thickness of material. In the case of a perforated plate with holes drilled at right angles to the surface the length of each hole is equal to the thickness of the plate. The coefficient of the thickness term in the resistance expression for such regular plates simplifies to the ratio of the total

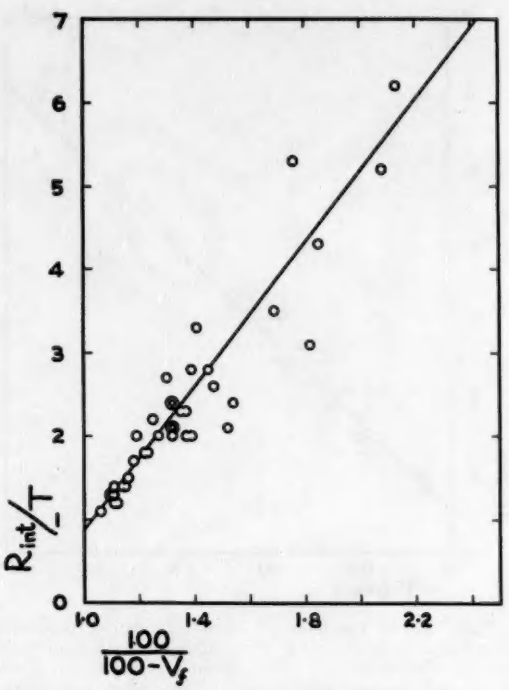

Fig. 8. Relationship between internal resistance per unit thickness and the reciprocal of fractional air volume in fabrics.

area of the plate to the area of the holes. For present purposes it is more useful to express this ratio as the total volume of the plate divided by the volume of the holes or air spaces within it; in the case of a fabric the corresponding value would be $100/(100 - V_f)$, where V_f is the percentage fiber volume. For reasons already referred to, however, the coefficient of the thickness term in the case of a fabric cannot be expected to equal this quantity. Since the pores or air spaces within a fabric do not proceed directly from one face to the other, a difference in fiber volume between two fabrics, besides indicating a difference in cross section of the pores, indicates as well a difference in length of the air passages, an effect which does not exist in the case of metal plates. In addition the probable existence of "cul-de-sacs" and variation of the cross-sectional area of channels along their length have already been mentioned. Consequently on two accounts the internal resistance of a fabric might be expected to exceed any computed value of $[100/(100 - V_f)]T$. Assuming for the present that the fiber transmits a negligible amount of

vapor, the extent to which the internal resistance of a fabric is increased over that of a regular uniformly drilled plate having the same solid-to-air ratio can be studied in the following way. Accepting 0.5 mm as an approximation to the external-resistance value for a fabric, the internal resistance R_{int} can be taken as $(R - 0.5)$ mm. This use of the same value for the external resistance of all fabrics will necessarily introduce some error, but it can be assumed that 0.5 mm is likely to be close to a representative value. The coefficient of the thickness term will therefore be $(R - 0.5)/T = R_{int}/T$, where R and T are expressed in millimeters. The corresponding coefficient to comply with the plate formula (22) would be equal to $100/(100 - V_f)$. When values of R_{int}/T were plotted against corresponding values of $100/(100 - V_f)$ a linear trend was indicated. While the majority of points lay along a straight line, there were a number of points scattered at some distance from it. These points were observed to correspond with fabrics possessing air permeabilities greater than 190 or less than 10. The former group lay below the line, while the latter lay above it. However, this behavior was not without exception; several fabrics in these extreme air-permeability ranges lay on the line. It had been realized that vapor diffusion in a fabric would depend not only on thickness and percentage fiber volume but probably on the particular fiber distribution in a fabric as well. This latter feature is not indicated with certainty by any readily measurable property of a fabric, but it is possible that unusual cases of fiber distribution are evidenced by extremes of air permeability. In Figure 8 is shown R_{int}/T plotted against $100/(100 - V_f)$ for fabrics having air permeabilities in the range 10 to 190.

The trend of the points in this graph can be represented by the line

$$\frac{R_{int}}{T} = 4.3\left(\frac{100}{100 - V_f}\right) - 3.4 \qquad (28)$$

which can also be written in the form

$$\frac{R_{int}}{T} = \frac{100}{100 - V_f}(0.9 + 0.034V_f) \qquad (29)$$

This equation shows the increasing ratio of the resistance of a fabric to that of a plate of the same solid content as the percentage fiber volume increases. In connection with the equation of the line, however, it will be observed that when V_f equals zero the value of R_{int} becomes equal to $0.9T$. This arises from the fact that a constant value of 0.5 mm for the external resistance was taken as applicable to all fabrics, whereas in actual fact this external resistance must be a variable dependent upon V_f, and must vanish when $V_f = 0$. In addition to demonstrating the increase in resistance with increase in fiber volume, the above empirical equation can be usefully employed to identify fabrics which deviate largely from it and thereby aid in seeking a further property relating to fiber distribution which can influence vapor diffusion.

In Table X, columns 2 and 3, are listed the values for R_{int}/T and $100/(100 - V_f)$ for all the fabrics examined. In column 4 are the calculated values for total resistance of the fabric using the equation

$$R = \frac{100}{100 - V_f}(0.9 + 0.034V_f)T + 0.5 \qquad (30)$$

In column 5 these calculated values are compared with the experimentally determined values given in Table VIII. In 61% of the fabrics tested, the differences do not exceed 0.2 mm and 84% do not differ by more than 0.5 mm. Those differing by more than 0.5 mm. are the fabrics previously referred to, which showed a large scatter in the general plot of R_{int}/T against $100/(100 - V_f)$. Of the fabrics which had low resistances and high air permeabilities, two were open-mesh materials made from heavy monofilament yarns (Saran and polyethylene fabrics) whose divergence from an average behavior for fabrics of similar thickness and percentage fiber volume was to be anticipated. The remainder of this group were knitted structures. The fabrics which had high resistances and very low air permeabilities were, however, more difficult to distinguish visually by any peculiarity in structural form.

The Influence of Fiber Composition

In the preceding analysis of experimental results it has been assumed that the transmission of water vapor by a fabric takes place by diffusion through the air within the material and that the fibers themselves offer a negligible contribution in this respect. The validity of this assumption requires further examination, since, if the fiber contribution is significant, different types of fibers may be expected to show differences in behavior because of the differences in their moisture-absorption characteristics.

The existence of an external-resistance term in the total resistance of a fabric necessarily implies that a fabric is heterogeneous with regard to moisture-vapor transmission. The extent of the heterogeneity cannot, on the basis of the information available, be quantitatively deduced from the magnitude of this external resistance, but the fact that the external resistance for fabrics does not differ greatly from the value found for a fritted glass disc having a 53% solid material content would suggest that the amount of water vapor transmitted by the fibers must be very small in relation to that which diffuses through the air between them. The same conclusion may be reached by a consideration of that part of the resistance which is dependent upon thickness. It has been shown that this internal resistance exceeds that of a regular perforated metal plate of the same solid content, and this increase has been attributed to the difference between the disposition of the fibers in a fabric and that of the solid material in a metal plate of the configuration studied. The coefficient of the thickness term indicated for fabrics having percentage fiber volumes in the range 20–29% (see Figure 7) is 2.25. For a perforated plate of 25% solid content the value would be 1.33 (equation 21). The ratio of these coefficients for fabric and perforated metal plate is 1.69. For higher percentage fiber volumes it will be recognized from Figure 8 that this ratio will increase, and its magnitude is indicative of little moisture being transmitted by the fiber.

In this connection some experiments on the resistance to passage of water vapor through layers of impermeable particles are of interest. For the purpose, particles of aluminum oxide were chosen and carefully screened to approximate a mesh size of 0.35 mm. A fritted glass disc was introduced into the testing apparatus in the place normally occupied by the test specimen. This disc supplied a bed upon which layers of the oxide particles could be built up to any desired thickness, and the resistance of the combination of disc plus a layer of oxide particles could be measured in the normal way. By varying the thickness of the particle layer, the increase in internal resistance R_{int} with thickness T could be determined. A slight tapping of the layer during mounting served to shake the particles down to a uniform degree of packing. Checks of the bulk density of the layer and the density of the oxide particles indicated the volume occupied by the particles to be 53% of the total volume. In Figure 9 are shown the results of these experiments, the intercept on the resistance axis in this case including the resistance of the fritted glass disc. The increase in

TABLE X

1 Fabric No.	2 $\frac{R_{int}}{T}$	3 $\frac{100}{100-V_f}$	4 R_{calc} (mm)	5 $R_{expt}-R_{calc}$ (mm)
1	2.6	1.47	1.4	−0.1
2	2.4	1.32	1.4	0.1
3	2.0	1.32	1.6	−0.1
4	2.8	1.45	1.9	0.3
5	2.0	1.37	2.1	−0.2
6	2.1	1.32	2.3	−0.1
7	2.1	1.32	2.6	−0.1
8	2.5	1.39	1.8	0.0
9	2.7	1.37	2.5	0.2
10	2.2	1.25	2.2	0.3
11	2.8	1.32	2.6	0.5
12	2.7	1.41	3.0	0.1
13	2.4	1.41	3.6	−0.2
14	2.0	1.27	2.4	0.0
15	1.4	1.11	1.9	0.0
16	2.1	1.41	3.0	−0.5
17	0.8	1.16	1.8	−0.6
18	0.3	1.14	1.7	−1.0
19	2.0	1.19	2.4	0.4
20	0.7	1.11	2.1	−0.8
21	2.3	1.37	3.0	−0.1
22	1.8	1.23	3.0	−0.1
23	2.4	1.32	5.6	0.4
24	2.0	1.39	0.9	−0.1
25	6.2	2.13	1.2	0.1
26	2.4	1.54	1.3	−0.2
27	2.1	1.52	1.1	−0.2
28	5.3	1.76	1.3	0.2
29	1.9	1.23	1.3	0.0
30	2.8	1.39	1.9	0.2
31	5.2	2.08	5.1	−0.2
32	2.3	1.35	1.5	0.0
33	1.5	1.54	0.9	−0.2
34	8.7	1.92	1.3	0.6
35	3.5	1.69	1.1	0.0
36	2.5	1.27	0.9	0.1
37	2.8	1.59	1.3	−0.1
38	4.3	1.85	1.8	0.0
39	1.8	1.37	1.6	−0.3
40	2.7	1.30	1.8	0.3
41	5.6	1.64	3.9	1.9
42	0.9	1.23	2.3	−0.9
43	3.1	1.82	3.8	−1.0
44	3.3	1.41	0.9	0.1
45	11.4	1.67	1.3	1.7
46	2.2	1.27	3.5	0.3
47	1.2	1.12	3.1	−0.3
48	1.4	1.15	4.2	−0.3
49	1.4	1.14	5.5	−0.2
50	1.3	1.11	7.6	−0.1
51	1.2	1.11	7.5	−0.4
52	1.5	1.16	13.1	0.2
53	1.8	1.22	17.4	0.1
54	1.1	1.06	13.6	0.1
55	1.3	1.10	17.4	0.2
56	1.7	1.18	22.7	0.9
57	1.3	1.10	20.2	0.3

TABLE XI

Test Specimen	T (mm)	R (mm of air)	R/T
Nylon film	0.04	85	2,100
Polyethylene film	0.05	4300	86,000
Cellophane, plain, transparent	0.03	1.3	43

resistance offered by an increasing thickness of particle layer is given by the value $3.48T$. The corresponding value for a perforated metal plate having a 53% metal content would be $2.12T$, and the ratio of the internal resistances for a particle layer and a plate of equal thickness is therefore 1.64. This is somewhat less than the comparable ratio for a fabric and perforated metal plate of much lower solid content (25%) computed above and lends further support to the view that little moisture is transmitted by the fibers.

More direct information on moisture transmission was obtained by a study of continuous films of regenerated cellulose (cellophane), nylon, and polyethylene. To simulate vapor transmission through rayon the sample of cellophane procured was, of course, the plain transparent type not treated to render it specially moistureproof. The results of tests on films are shown in Table XI.

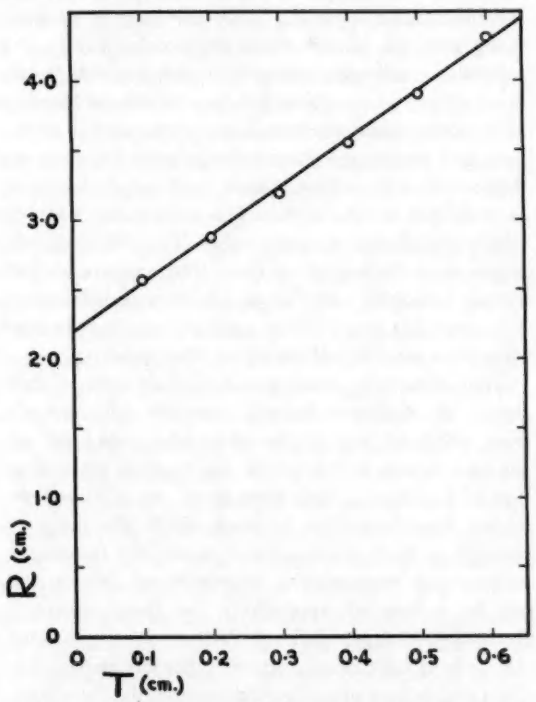

Fig. 9. The resistance of layers of aluminum oxide particles resting on a fritted glass plate increases linearly with thickness.

TABLE XII

	Equivalent Resistance (mm air)	Gradient (% R.H.)	Range (% R.H.)
Air layer below sample	10.0	19.1	80.9–100
Cellophane	1.3	2.5	78.4– 80.9
External air layer	7.0	13.4	65.0– 78.4

It will be seen that there are very marked differences in the permeabilities of the films of nylon, polyethylene, and cellophane which place them in the order of their moisture-absorptive capacities. Even in the case of the most permeable film, however, its resistance is forty-three times greater than that of an equal thickness of air, and the contribution of any fibers to the transmission of water vapor through a fabric would therefore appear to be of a very low order.

Some reference should, however, be made to the actual moisture condition of the fibers and films under which the resistance to water-vapor transmission was measured. The results on films show marked differences in resistance with materials of different moisture-absorptive capacities, and, because the moisture contents of hygroscopic fibers such as wool, rayon, and cotton increase with an increase in the relative humidity of the air with which they are in equilibrium, it is to be anticipated that absorbent fibers will show a decrease in resistance as moisture content increases. That this is so is indicated by results obtained by Fourt and Harris [3]. In the experiment quoted in Table XI, the resistance of cellophane was measured with the film mounted 1 cm above a water surface, and a vapor pressure in the ambient air equal to 65% R.H. The total vapor-pressure gradient is therefore equivalent to 35% R.H. at 21°C, and the gradients in the several layers may therefore be listed in accordance with their resistances as shown in Table XII.

The resistance which was found to be forty-three times that of an equal thickness of air is that of cellophane which is in equilibrium with an atmosphere of 78.4% R.H. on one face and 80.9% on the other, or approximating a moisture condition which would be in equilibrium with an atmosphere of 80% R.H. A similar experiment by Fourt and Harris on cellophane, in which the vapor pressures on the two sides of the specimen were equal to 72.9 and 76.6% R.H.,

gave a result in which the resistance was found to be forty times that of an equal thickness of air, a satisfactory check with the above value. In a second experiment, by a method employing a drying agent instead of water to produce a vapor-pressure gradient, these authors found the resistance of the same cellophane to be twelve hundred times that of an equal thickness of air when the vapor pressures on the two sides of the specimen corresponded to 4% and 61% R.H. In this case the vapor-pressure gradient through the cellophane is too great to regard the material as being in approximate equilibrium with the mean of these two humidity values, but it is evident that there is a large change in resistance with change in the equilibrium-moisture condition of the sample. Further experiments are required to produce better quantitative information on this point. The general conclusion may be drawn, however, that the contribution of the fibers to the transmission of water vapor by a fabric is negligibly small, with the possible exception of very densely woven materials made from the more hygroscopic fibers under conditions of very high moisture content.

Further direct confirmation of this conclusion was sought through measurements made on a specially constructed series of fabrics when these were in equilibrium with approximately 75% R.H. This series of fabrics comprised wool, cotton, viscose rayon, and nylon, spun and woven to structures as nearly identical as possible with respect to fiber size, fabric construction, and percentage fiber volume. To this end the fibers of wool, nylon, and rayon were chosen to be of approximately the same diameter and length. This was achieved by using a 60's quality wool, a 6-den 4-in. staple nylon, and an 8-den 4-in. staple viscose rayon. The cotton could not, of course, be made to match the others with respect to fiber dimensions. Yarns from each were then spun to counts giving as closely as possible the same volume of fiber for equal lengths of yarn. The wool, nylon, and rayon all were spun on the worsted system, and the actual counts spun in each case were: wool—2/31's worsted counts; nylon—2/36's worsted counts; rayon—2/27½'s worsted counts; cotton—2/18's cotton counts.

In addition the wool was also spun to 1/16's so as to introduce a comparison of singles versus 2-ply yarn of equivalent counts. The four twofold yarns were beamed to form a separate warp of each, and pieces were woven using all five yarns as filling.

TABLE XIII

Warp	Weft	Thickness $p=0.05$ psi (mm)	Fiber Volume (%)	Resistance (mm)
Cotton	Cotton	0.84	26	2.3
	Nylon	0.88	25	2.4
	Rayon	0.77	27	2.2
	Worsted (2-ply)	0.91	25	2.3
	Worsted (singles)	0.88	24	2.3
Nylon	Cotton	0.86	25	2.3
	Nylon	0.86	23	2.2
	Rayon	0.83	24	2.3
	Worsted (2-ply)	0.88	25	2.6
	Worsted (singles)	0.95	22	2.5
Rayon	Cotton	0.84	26	2.7
	Nylon	0.86	23	2.6
	Rayon	0.76	26	2.3
	Worsted (2-ply)	0.89	24	2.6
	Worsted (singles)	0.93	21	2.5
Worsted (2-ply)	Cotton	0.89	25	2.1
	Nylon	0.93	24	2.2
	Rayon	0.85	25	2.2
	Worsted (2-ply)	0.92	25	2.6
	Worsted (singles)	0.88	25	2.2

In this way 20 samples of fabric were prepared, with the weave and ends and picks per inch in all cases being kept the same. Finishing consisted only of a mild scour, tentering, and a light pressing. Although every effort was made to produce fabrics as identical as possible, some uncontrollable variations in thickness and percentage fiber volume were found in the finished fabrics. These were not large, however, as indicated by the figures given in Table XIII, in which are shown also the values found for the resistances of the twenty fabrics. The weights of cloth averaged roughly at 8.5 oz/sq yd, these weights varying somewhat from one to another because the constructions were based on equal fiber volumes.

The relatively nonhygroscopic all-nylon fabric shows no higher resistance than the fabrics made from 100% of any of the other fibers, and the resistance values of the whole series gives no indication of correlation with fiber type. It is to be concluded, therefore, that, at least within the range of percentage fiber volumes most commonly found, the water-vapor transmission properties of fabrics will not be influenced appreciably by their moisture-absorption characteristics. As previously pointed out, only in the case of extremely densely woven fabrics (which as a group would necessarily have comparatively high resistances in relation to their thickness) would the nature of the constituent fibers be

at all likely to make its influence felt, and then only under conditions of very high humidity.

Summary and Conclusions

Two component resistances are distinguished which together constitute the total resistance of a fabric to the transmission of water vapor by diffusion: (1) that resistance which results from the presence, in the path of vapor flow, of a surface which is heterogeneous in its vapor-transmission properties; and (2) the resistance to passage of vapor from one surface of the fabric to the other, i.e., within the fabric itself. The magnitude of the former resistance, unlike the latter, is independent of the thickness of the material.

The resistance which arises from the presence of a partial barrier obviously varies from zero to infinity as the amount of impenetrable material in the surface varies from 0 to 100%. The precise value of this resistance is not, however, determined simply by the ratio of total impenetrable to total penetrable areas, but is highly dependent upon the size and distribution of the individual penetrable areas in the surface. For fabrics in the range of 20–29% fiber volume this resistance component has been found to approximate 0.5 mm of still air.

It is important to realize the significance of the two parts constituting the total resistance of a fabric, the one associated only with surface geometry and the other associated with fabric thickness. In the case of a very thin fabric, the former may be the dominant term, while in a thick fabric its contribution to the total resistance will be relatively small. A thin fabric will therefore possess a proportionately higher resistance for its thickness than a thick fabric of similar structure and percentage fiber volume, and any comparison of fabrics on the basis of resistance per unit thickness is therefore inadmissible and likely to be misleading.

The resistance of fibers to transmission of water vapor, as indicated by experiments on thin films, show large differences. Lower resistances are exhibited by more hygroscopic materials, and resistance increases in the order of decreasing moisture-absorption capacity. Even those fibers which have the highest moisture-absorption characteristics, however, have resistance so much greater than the resistance of air that in any ordinary fabric the whole of the moisture transmission can, without appreciable error, be regarded as taking place by diffusion though the air spaces only, and the fibers, whatever their type, considered to be impermeable. Only in the very densest fabrics under conditions of very high humidity would the validity of this conclusion be questionable.

Because the fibers themselves contribute little to vapor transmission, the most important variable concerned in fabric resistance is the quantity of fiber present. Variation in quantity of fiber may exhibit itself in two ways: in thickness of fabric or in percentage fiber volume. There is no reason to doubt that that part of the total resistance associated with the diffusion of vapor within the fabric itself is proportional to thickness. The influence of percentage fiber volume is more complex. An increase in percentage fiber volume means a correspondingly reduced permeable portion through which vapor may diffuse. In the case of uniformly drilled metal plates it has been shown that the coefficient of the thickness term in the resistance expression is simply the ratio of the total area to the area of the perforations. A fabric, however, does not in general provide a structure in which holes proceed directly from one face to the other, but may better be thought of as an interlacing mass of fibers, to pass through which water-vapor molecules are required to follow a tortuous path. This path length increases per unit thickness of fabric as the percentage fiber volume increases; and in addition the path cross section decreases with increase of fiber volume. It follows that, in two fabrics of equal weight made from the same raw material, it is possible to have resistances which are nearly the same although one fabric may be considerably thicker than the other.

Experimental data indicate that the spatial distribution of fibers in a fabric may have a marked influence on resistance, and it is probable that any expression for resistance which does not take account of a number of variables will fail to provide accurate values. While an empirical equation can be derived which will indicate the mean trend in resistance values with changes in the important variables of thickness and percentage fiber volume, the precise resistance for any particular cloth cannot be deduced with certainty from these data alone, and in some cases the deviations may be large. It has been shown in the analysis of the results presented that where large deviations do occur between experimental and calculated values, the fabrics possess very high or very

low air permeabilities, a fact which itself indicates the influence of the geometry of fiber distribution.

Fabrics in general possess low resistance to water-vapor diffusion due to their large content of free air space. Because the movement of water vapor through a fabric is confirmed entirely to the air spaces within it, it is readily understood that the application of any coating to a fabric is likely to cause a large increase in vapor resistance. The fact that the resistance of fabrics and air are of the same order for equal thicknesses also has an important bearing on the total resistance of a clothing assembly. For example, the resistances of a knitted underwear fabric, a cotton shirting material, and a wool uniform cloth may together comprise only a resistance equivalent to 0.5 cm of still air. Under still conditions, however, the resistance of a clothing assembly of which these fabrics are the components may be several times this amount, due to the resistance of the air layers included with the fabrics in the assembly. For this reason, a reduction in the number of layers of clothing is very much more effective in assisting the diffusion of water vapor away from the skin than would be indicated by the sum of the resistances of the fabrics themselves. More precise knowledge of the distances which normally exist between different layers of fabrics when worn as clothing would be valuable. In actual service, of course, diffusion in clothing is assisted by air interchange, which depends upon both fabric structure and garment design. Other factors also enter into the best choice of clothing for particular purposes, but the consideration of such factors is beyond the scope of this report.

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Appendix I

Resistances of Perforated Metal Plates

d (cm)	T (cm)	R (cm of still air)								
		$N=7$	$N=19$	$N=55$	$N=151$	$N=421$	$N=1123$	$N=1743$	$N=1980$	$N=5450$
0.0583	0.0508	312	97	35.2	12.3	4.29	—	—	0.76	0.27
	0.0787	340	134	43.6	16.3	5.70	—	1.15	—	—
0.0905	0.0279	—	—	14.1	—	1.60	—	—	—	—
	0.0508	141	50	18.0	6.20	2.04	0.72	—	—	—
	0.0787	—	—	21.9	—	2.71	—	—	—	—
	0.165	299	101	34.1	12.1	4.46	1.55	—	—	—
	0.264	—	—	48.7	—	6.49	—	—	—	—
	0.485	—	—	76	—	—	—	—	—	—
0.158	0.0508	59	22.0	7.74	2.48	0.76	0.24	—	—	—
	0.165	79	36.4	12.5	4.43	1.45	0.51	—	—	—
0.247	0.0279	—	—	3.42	—	0.22	—	—	—	—
	0.0508	36.0	12.7	3.96	1.20	0.29	—	—	—	—
	0.0787	—	—	4.49	—	0.35	—	—	—	—
	0.165	46	19.0	6.21	2.02	0.59	—	—	—	—
	0.264	—	—	8.40	—	0.86	—	—	—	—
	0.401	—	—	11.0	—	—	—	—	—	—
	0.485	—	—	12.3	—	—	—	—	—	—
	0.610	—	—	15.0	—	—	—	—	—	—
	0.711	—	—	17.1	—	—	—	—	—	—
0.410	0.0508	17.5	5.90	1.73	0.40	—	—	—	—	—
	0.165	24.8	8.75	2.57	0.71	—	—	—	—	—

Appendix II

The fabric construction particulars given are those actually determined on the finished cloths, except for the quoting of nominal yarn deniers.

Identification	Weave	Ends per Inch	Picks per Inch	Warp Yarn*	Weft Yarn*	Weight (oz/sq yd)	Air Permeability
1. Cotton	Plain	72	60	1/23 c	1/20 c	4.5	18
2. Cotton	2/1 twill	97	70	1/34 c	1/24 c	4.4	65
3. Cotton, chambray	Plain	78	57	1/20 c	1/20 c	5.5	42
4. Cotton, drill	3/1 twill	115	53	1/18 c	1/12 c	8.3	12
5. Cotton, drill	3/1 twill	114	56	1/18 c	1/12 c	8.2	16
6. Cotton, drill	5/1 twill	96	40	1/12 c	1/12 c	8.8	18
7. Cotton, drill	5-end sateen	97	44	1/13 c	1/7 c	9.9	21
8. Cotton	Oxford	170	65	3/72 c	2/50 c	6.7	1.2
9. Cotton, duck	Plain	88	31	1/9 c	1/9 c	10.2	4.2
10. Cotton, duck	Plain	52	32	2/15 c	2/15 c	8.2	20
11. Cotton, duck	Plain	52	38	2/13 c	2/16 c	10.2	5.8
12. Cotton, duck	Plain	51	35	2/13 c	3/13 c	12.5	3.1
13. Cotton, duck	Plain	49	33	3/13 c	3/13 c	15.3	2.0
14. Cotton, ticking	3/1 herringbone	79	64	1/12 c	1/12 c	8.6	15
15. Cotton, flannelette	Plain	46	38	1/27 c	1/9 c	4.6	80
16. Cotton, canvas	Plain	46	27	3/13 c	3/13 c	12.5	5.5
17. Cotton, knit double	Plain knit	Wales 28	Courses 38	1/30 c		5.3	310
18. Cotton	Warp knit	Wales 30	Courses 32	1/40 c		4.3	275
19. Cotton/viscose and hair	Plain	47	23	1/6 c	1/5 c	8.3	20
20. Cotton and wool	Plain knit	Wales 17	Courses 22	1/10 c		5.3	389
21. Wool, serge	2/2 twill	62	38	2/26 w	1/8 w	10.7	42
22. Wool	2/2 twill	64	64	2/30 w	2/22 w	10.0	18
23. Wool, melton	2/2 twill	36	32	1.3 r	1.1 r	21.9	16
24. Silk, crepe	Plain	126	94	—	—	1.7	65
25. Acetate, filament	5-end sateen	202	94	75 d	75 d	2.7	66
26. Acetate/viscose filament	Plain	110	69	125 d	150 d	3.7	86
27. Viscose, filament	Plain	77	64	150 d	150 d	2.9	139
28. Viscose, filament	2/2 twill	116	66	150 d	150 d	3.6	38
29. Viscose, spun	Plain	77	66	1/30 c	1/30 c	3.8	192
30. Viscose, spun	Plain	48	40	2/16 c	1/10 c	7.1	116
31. Viscose, filament	Matt	40	36	1650 d	1650 d	19.0	33
32. Viscose filament/cotton	8-end sateen	148	70	150 d	1/18 c	5.2	41
33. Nylon	Plain	88	87	70 d	70 d	1.5	323
34. Nylon	Plain	160	88	70 d	70 d	2.6	6.9
35. Nylon	Plain	155	84	70 d	70 d	2.3	12
36. Nylon, marquisette	—	74	42	70 d	70 d	1.4	Very high
37. Nylon	5-end sateen	315	104	40 d	70 d	3.1	220
38. Nylon	3/1 twill	238	72	3/70 d	70 d	4.7	60
39. Nylon	Open net	60	56	260 d	260 d	3.9	392
40. Nylon	2/2 twill	—	—	70 d	Spun	4.7	77
41. Orlon	Plain	54	30	1100 d	1100 d	12.8	2.2
42. Saran	Plain	12	12	2920 d	2920 d	9.2	Very high
43. Polyethylene	3/1 twill	93	34	540 d	540 d	9.1	188
44. Glass	Plain	62	58	—	—	3.3	25
45. Glass	Plain	43	32	1/8 c	1/8 c	6.6	2.5
46. Glass	2/2 twill	26	35	2-ply	2-ply	24	7.5
47. Felt, wool, hair	—	—	—	—	—	7.9	125
48. Felt, wool, hair	—	—	—	—	—	13.1	42
49. Felt, wool, hair	—	—	—	—	—	19.6	39
50. Felt, wool, hair	—	—	—	—	—	19.8	44
51. Felt, wool, hair	—	—	—	—	—	20.3	30
52. Felt, wool, hair	—	—	—	—	—	45	53
53. Felt, wool, hair	—	—	—	—	—	67	10
54. Felt, wool, hair	—	—	—	—	—	30	44
55. Felt, wool, hair	—	—	—	—	—	50	23
56. Felt, wool, hair	—	—	—	—	—	83	10
57. Felt, wool, hair	—	—	—	—	—	55	10

* c = cotton count; w = worsted count; r = woolen run; d = denier.

Entropy Changes Accompanying the Stretching of Cellulose Fibers in Water[1]

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Abstract

Thermodynamic equations for elasticity are used to relate the force-temperature behavior of cellulosic fibers in water to the entropy of stretching. Water-fiber interactions may have an appreciable influence on the observed behavior, but this cannot be decided without further experimental data on the swelling and sorption behavior of cellulose in water. A transition in the elasticity of textile viscose rayon occurs in water at about 45°C, with a negative entropy of stretching (rubberlike elasticity) being found above the transition temperature. Alkali swelling of viscose rayon causes an increase in rubberlike elasticity and a lowering of the transition temperature. The elasticity of cotton is primarily due to energy forces, and no marked change after mercerization is found over the temperature range from 5° to 80°C. Comparison of highly oriented cellulose acetate experimental samples before and after saponification shows that the acetate side groups cause a lower temperature of transition to rubberlike elasticity, due to a reduction in intermolecular attractions. Commercial-type cellulose acetate fibers show effects of extension on elastic behavior which indicate complex structural changes in the fiber as it is being stretched.

Introduction

Two main classes of elastic solids are now recognized as possessing basically different modes of deformation. On the one hand there are crystalline substances with glasslike behavior in which the restoring force upon deformation is due to distortions of the normal bond distances and angles, that is, to an energy mechanism. On the other hand there are amorphous, rubberlike materials in which the restoring force is due to the tendency of the molecular chains to return from their extended form into the statistically preferred, randomly coiled configuration of high entropy. In this latter case elasticity is said to be due to an "entropy mechanism."

Textile fibers, which are composed of both crystalline and amorphous elements,[4] present a case intermediate between the two classes of elastic solids mentioned above. In the crystalline regions, elastic forces are primarily due to energy changes, whereas in the amorphous regions the greater freedom of motion causes entropy changes to be of greater relative importance. In cases such as cellulose fibers, in which there are strong attractions between neighboring chains, rubberlike behavior is manifested only at elevated temperatures. It would seem reasonable, therefore, to use the temperature of transition from glasslike to partial rubberlike elasticity as a measure of the strength of intermolecular attractions in the amorphous regions. Furthermore, a study of the magnitude of entropy changes occurring when a fiber is stretched at various temperatures and to various extents should shed light on the mechanism of

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[4] The terms "crystalline" and "amorphous" are used in this paper to denote those portions of the material which are of high and low order, respectively, as defined by Howsmon and Sisson in Chapter IV–B on "Submicroscopic Structure of Cellulose" in Ott and Spurlin (eds.), *Cellulose and Cellulose Derivatives*, Vol. I, Interscience, New York, 2nd ed. (1954).

deformation in the amorphous fraction. The effects of side groups or of chemical treatments on the rubberlike behavior of the fiber should aid still further in the definition of deformation processes.

The present paper is concerned with a description of the application of force-temperature measurements to the evaluation of energy and entropy changes which occur when cellulosic fibers are stretched in water, and with interpretation of the results obtained.

Thermodynamic Basis of Force-Temperature Measurements

The contributions of energy and entropy changes to the force necessary to stretch a fiber can be determined by measuring the temperature coefficient of the force necessary to maintain the fiber at constant length. This fact was first brought out in the thermodynamic equations for elasticity derived by Wiegand and Snyder [18]. Their equations have been modified by Elliott and Lippmann [6] and were recently reviewed by Katz [9].

The first law of thermodynamics for fiber stretching can be written

$$dE = T\,dS + f\,dl \tag{1}$$

In this equation f is the force on the fiber, l is the fiber length, $f\,dl$ is the work done on the fiber in stretching it an amount dl, and E, T, and S are the internal energy, absolute temperature, and entropy, respectively.

At constant temperature and pressure, equation (1) can be differentiated with respect to the fiber length to give

$$(\partial E/\partial l)_{T,P} = T(\partial S/\partial l)_{T,P} + f \tag{2}$$

Substitution of the Helmholtz free-energy definition in differential form ($dA = dE - T\,dS - S\,dT$) into equation (1) gives $dA = f\,dl - S\,dT$, from which it can be shown that

$$(\partial S/\partial l)_{T,P} = (\partial^2 A/\partial l\,\partial T) = -(\partial f/\partial T)_{l,P} \tag{3}$$

Substitution of equation (3) into equation (2) gives upon rearrangement

$$f = (\partial E/\partial l)_{T,P} + T(\partial f/\partial T)_{l,P} \tag{4}$$

or

$$f = f_E + f_S \tag{5}$$

The total force on a filament held at fixed length is, thus, expressed in terms of its energy and entropy components. Any two of the three terms in equation (4) are needed for this separation of the net force. In the present work, the net force, the equilibrium force-temperature coefficient $(\partial f/\partial T)_{l,P}$, and the temperature are the measured quantities. The value of f_E can then be calculated by difference from equation (5).

It can be seen from equation (3) that a positive force-temperature coefficient, or positive value of f_S, implies a decrease in entropy, or an increase in the degree of order, as the specimen is stretched. In this case the deformation is predominately rubberlike and any glasslike deformation occurring is relatively small in comparison with the rubberlike deformation. If the force-temperature coefficient is negative, entropy increases with stretching, the rubberlike deformation is relatively small, and the material exhibits glasslike elasticity. The negative force-temperature coefficient probably occurs simply as a result of thermal expansion, which can be interpreted as an entropy increase due to deformation of bond distance and angles from their more probable values. A disordering effect or an increase in volume on stretching would also lead to a positive entropy of stretching [10].

Effect of Water on the Entropy of Stretching Cellulose Fibers

In the present work, and in most of the earlier efforts in the field, measurements were carried out with the cellulose filaments immersed in water. Application of the thermodynamic equations presented above, however, is based on the assumption that no change in moisture content of the specimen being tested occurs when the temperature is changed. This assumption is not justified for the case of cellulose fibers. It is of interest, therefore, to consider the possible influence of changes in water content on the observed force-temperature behavior.

The basic thermodynamic equations for elasticity have been extended to two-component systems by Katz [9], who showed that the force-temperature coefficient corrected to constant composition is related to the observed coefficient by the relation

$$(\partial f/\partial T)_{l,P,n_1} = (\partial f/\partial T)_{l,P} - (\partial f/\partial n_1)_{T,P,l}(\partial n_1/\partial T)_{l,P} \tag{6}$$

where n_1 is the number of moles of water present in the specimen.

White [17] has also considered the influence of water-polymer interaction on the observed force-temperature behavior. His treatment, while simi-

lar to that of Katz, makes use of the fact that the chemical potential of the water in the polymer must be equal to that of liquid water. The following equation has been derived by White [17]:

$$(\partial f/\partial T)_{P,l,n_1} = (\partial f/\partial T)_{P,l,\mu_1=\mu_1^0} + \left\{ \frac{(\partial l/\partial n_1)_{T,P,f}}{(\partial l/\partial f)_{T,P,\mu_1} - (\partial l/\partial n_1)_{T,P,f}(\partial n_1/\partial f)_{T,P,\mu_1}} \times \left[\frac{-(\partial \mu_1/\partial T)_{P,l,n_1} - \bar{S}_1^0}{(\partial \mu_1/\partial n_1)_{T,P,l}} \right] \right\} \quad (7)$$

where n_1 is the number of moles of sorbed water; μ_1 is the chemical potential of the sorbed liquid; μ_1^0 and $\bar{S}_1^0$ are the chemical potential and partial molal entropy, respectively, of pure liquid water; $(\partial f/\partial T)_{P,l,n_1}$ is the force-temperature coefficient for constant solid phase composition, i.e., the coefficient after correction for the effect of the change in swelling with temperature; and $(\partial f/\partial T)_{P,l,\mu_1=\mu_1^0}$ is the experimentally determined force-temperature coefficient for the specimen immersed in liquid water.

Data suitable for evaluation of the swelling correction terms in equations (6) and (7) for fibers immersed in water are not available in the literature. However, data at other humidities have been used to estimate all but one of the factors in equations (6) and (7), and these are presented along with evaluation procedures and comments in Table I. Data used were taken from the results of Treloar [14] on the change of moisture content with stress and on the longitudinal swelling of viscose rayon, Babbitt [2] on the entropy of sorption of water by cotton, and Urquhart and Williams [15] on the change of moisture content with temperature for cotton. The estimates in Table I are calculated for a 150-den cellulose filament 23 cm in length for comparison with the experimental results obtained on a multifilament-yarn of those dimensions.

All the factors in White's correction term [in brackets in equation (7)] are at least roughly estimated in Table I, from which a value of 0.2 g/°C for the correction term can be calculated. This value is by no means quantitative, for the estimate of 0.1 cal/deg/mole for the entropy term $[-(\partial \mu_1/\partial T) - \bar{S}_1^0]$ is an upper limit, and may be too large by one or more orders of magnitude. The value of the correction term would be correspondingly reduced. Also, errors in the estimates of $(\partial l/\partial n_1)_{T,P,f}$ and $(\partial n_1/\partial f)_{T,P,\mu_1}$ could lead to an error in the sign of the estimated correction.

One factor in the correction term of equation (6) could not be estimated from literature data. Only the sign of $(\partial f/\partial n_1)_{T,P,l}$ could be deduced. This is clearly negative, since both of the partial derivatives on the right-hand side of equation (8) are positive:

$$(\partial f/\partial n_1)_{T,P,l} = -(\partial f/\partial l)_{T,P,n_1}(\partial l/\partial n_1)_{T,P,f} \quad (8)$$

TABLE I. Factors Necessary for Evaluating Correction Term for Cellulose Fibers

All reduced to 150-den filament, 23 cm long; temperature = 25°C

Factor	How Evaluated	Estimate	Comments
$(\partial l/\partial n_1)_{T,P,f}$	From $(\partial l/\partial \mu_1) \times (\partial \mu_1/\partial n_1)_{T,P,f=0}$, estimated from Treloar's Figures 6 and 8, respectively, using $d\mu_1 = RT\, d \ln p/P$. Oriented cellulose values at R.H. = 100% estimated from ratios for isotropic and oriented cellulose at lower R.H. [14].	2×10^4 cm/mole	Large error in measuring slope of R.H. vs. length and R.H. vs. moisture content curves at 100% R.H. l and n_1 estimates at 100% R.H. probably in error. Data for viscose rayon.
$(\partial l/\partial f)_{T,P,\mu_1}$	Assumed Young's modulus of 10^{10} dyne-cm^{-2} for cellulose in water.	2×10^{-2} cm/g	Varies with extension and nature of specimen.
$(\partial n_1/\partial f)_{T,P,\mu_1=\mu_1^0}$	From Treloar's [14] Figure 4 on change of water content with tension for oriented viscose rayon at 75.5% R.H.	2×10^{-7} moles/g	Evaluated for 75.5% R.H. and may be quite different for cellulose in liquid water. Data for viscose rayon.
$(\partial \mu_1/\partial n_1)_{T,P,l}$	Taken equal to $(\partial \mu_1/\partial n_1)_{T,P,f=0}$, measured above.	4×10^5 cal/mole^2	Subject to same errors as $(\partial l/\partial n_1)_{T,P,f}$. Data for viscose.
$-(\partial \mu_1/\partial T)_{P,l,n_1} - \bar{S}_1^0$	No available data for evaluation at 100% R.H. Best estimates based on data of Babbitt [2] up to 95% R.H.	0.1 cal/deg/mole	Extrapolation of Babbitt [2] indicates value may be much smaller than quoted estimate. Data for cotton.
$(\partial n_1/\partial T)_{l,P}$	From data of Urquhart and Williams [15] at 95% R.H.	-10^{-7} mole/°C	Value in liquid water may be quite different. Data for cotton.

Since Table I indicates that $(\partial n_1/\partial T)_{l,P}$ is negative at 25°C (at least for cotton), a negative value for Katz's correction term $[-(\partial f/\partial n_1)_{T,P,l}(\partial n_1/\partial T)_{l,P}]$ is obtained.

Measurements on a viscose rayon filament of the dimensions assumed in the above calculations gave a value of the order of −0.01 g/°C for the force-temperature coefficient at 25°C (see Figure 2). This small magnitude in comparison with the estimated value of 0.2 g/°C for the correction term in equation (7), and the discrepancy in sign between the correction terms of equation (6) and (7), lead to the conclusion that available data in the literature are not suitable for evaluating the water-fiber interaction for fibers immersed in water.

The question of just how important a factor the water-cellulose interaction is in the force-temperature behavior will only be resolved by additional experimental evidence. More accurate swelling and sorption data for cellulose in water are needed before the swelling correction terms can be properly evaluated. In the force-temperature measurement, one feasible approach might be to work at a lower relative humidity where the necessary swelling and sorption data are already available. Another might be to hold the water content of the fiber specimen constant by varying the relative humidity as the temperature is changed.

In the interpretation of the results described below, it will be assumed that intermolecular attractions, rather than swelling changes, are primarily responsible for the observed behavior. Should it be shown later that the water-cellulose interaction is responsible for the observed behavior, the force-temperature method should prove of considerable value in studying the swelling and sorption characteristics of cellulose fibers.

Previous Results

The first force-temperature investigation on cellulose fibers was carried out by Meyer and Lotmar [12], who were not able to obtain the reversible measurements necessary for quantitative interpretation, but did report a negative force-temperature coefficient for ramie, Lilienfeld rayon, and viscose rayon over a limited temperature range. Cellulose acetate was stated to have a positive force-temperature coefficient although the effect was almost obscured by stress relaxation which occurred during the course of the temperature change.

Wakeham and Gerrow [16] found negative force-temperature coefficients for cotton and viscose rayon. Their values were obtained for a rapid temperature change from about 70°C to 5°C in one step, and a linear force-temperature relation was assumed. The results of Andersen [1] on the effect of temperature on the stiffness of cellulose fibers also indicate a negative force-temperature coefficient for cotton and viscose rayon.

Roseveare [13] has obtained reversible measurements on ramie and a variety of viscose rayon fibers. A negative force-temperature coefficient implying glasslike elasticity was found for ramie over the temperature range from 5° to 90°C. Textile and tire cord viscose rayon were found to have a minimum in the force-temperature relation near 45°C, with partial rubberlike behavior being found only above this temperature. Fibers of greater molecular orientation were found to have higher temperatures of transition from glasslike to rubberlike elasticity.

The present work extends the experimental measurements to cotton, alkali-swollen cotton and viscose rayon, cellulose acetates of various orientation, and saponified cellulose acetate.

Apparatus and Experimental Methods

A schematic representation of the apparatus used in the present investigation appears in Figure 1. The fiber or filament F was mounted between an upper hook and lower clamp atop the threaded rod R. The filament was tied and cemented with Glyptal enamel to the upper hook. A metal collar on the threaded rod supported a rubber stopper S, and concentric glass tubes surrounded the fiber. Whenever necessary, the glass tubes could be lowered by turning the collar down the threaded rod. The lower end of the threaded rod was mounted on the crosshead of the Instron tensile tester [7], and the upper hook was connected to the Instron load cell. By lowering the crosshead, the filament could be stretched to a predetermined length, and maintained there while the load was recorded continuously to within ±0.01 g. Temperature was recorded to within ±0.5°C by an iron-Constantan thermocouple placed in the water next to the filament. The temperature at the load cell remained constant within ±1°C over the course of a temperature cycle. A two-pen recorder was used to obtain simultaneous readings of force and temperature.

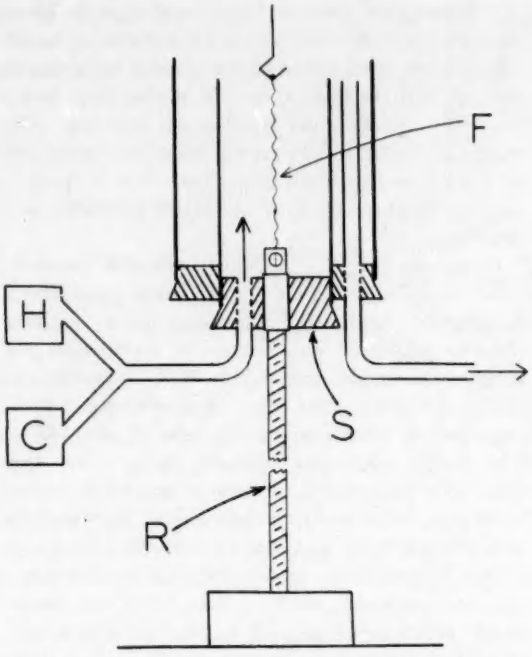

Fig. 1. Apparatus for measuring force-temperature behavior of filaments in water. Lettering explained in text.

The temperature of the filament was controlled by water circulated around the filament at a rate of approximately 350 ml per min. By adjusting the relative flow rates from hot and cold water reservoirs, denoted by *H* and *C* in Figure 1, temperatures from ca. 80°C to 8°C could be obtained.

Initial specimen lengths were measured under a tension of 10 mg per den in water at the highest temperature employed, using the dial gages of the Instron tester. Filament lengths of 8–10 in. were employed.

In order to minimize the effects of thermal expansion by the apparatus, the hooks leading from the specimen to the load cell and the threaded rod to which the lower end of the specimen was attached were constructed of Nilvar low-expansion alloy. The threaded rod was long enough to insulate thermally the metal crosshead of the Instron tester. The total expansion in the apparatus was determined using a calibrated spring in series with Nilvar hooks which lead from the load cell to the lower clamp. The linear expansion of the apparatus was then calculated from the spring force constant and deflection constant of the load cell and from the force change with temperature. The measured expansion of 2×10^{-6} in./°C was considered small enough to be neglected for lengths of specimens used in these tests.

TABLE II. Force Components of 150-Den Textile Viscose Rayon Yarn Calculated from Figure 2 at 70°C

Extension (%)	f_{total} (g)	f_S (g)	f_E (g)
1	1.96	1.10	0.86
3	7.18	1.30	5.88
6	19.37	1.30	18.07
10	42.02	1.30	40.72

When textile filaments are stretched and then held at fixed length, the retractive force decays gradually. The rate of this stress relaxation decreases with time, until eventually the force can be considered to be constant over short time intervals. Meyer and Ferri [11] first pointed out that a period of stress relaxation to such a "constant" force must be allowed before a reversible force-temperature cycle suitable for thermodynamic analysis can be obtained. Furthermore, the stress relaxation must be carried out at the highest temperature to be encountered; otherwise higher temperatures would increase the relaxation rate and prevent the attainment of a reversible force-temperature cycle. It was found experimentally that an initial relaxation of from 2–6 hr at 80°C was necessary to obtain a reversible cycle. The criterion for reversibility is that the force on the specimen be essentially the same before and after completion of a temperature cycle. With the apparatus used in the present investigations, a temperature cycle with ten or more intermediate temperatures between 80° and 8°C could be completed in about 30 min.

Results and Discussion

Viscose Rayon

The results obtained with a 150-den multifilament textile viscose rayon yarn spun with 38% godet stretch are shown in Figure 2. It can be seen that a transition in the force-temperature behavior occurs near 45°C. This result is similar to that reported for viscose rayon by Roseveare [13]. The transition here appears to be analogous to the second-order transition in rubber, although it is more gradual. Below the transition region, the elastic force is probably due to energy forces, i.e., to distortions of interchain hydrogen bonds in amorphous regions. Above

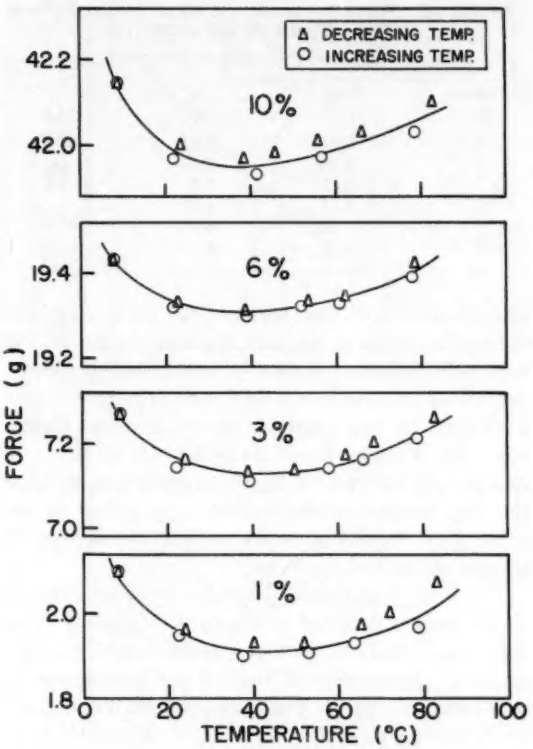

Fig. 2. Force-temperature behavior of 150-den textile viscose rayon yarn.

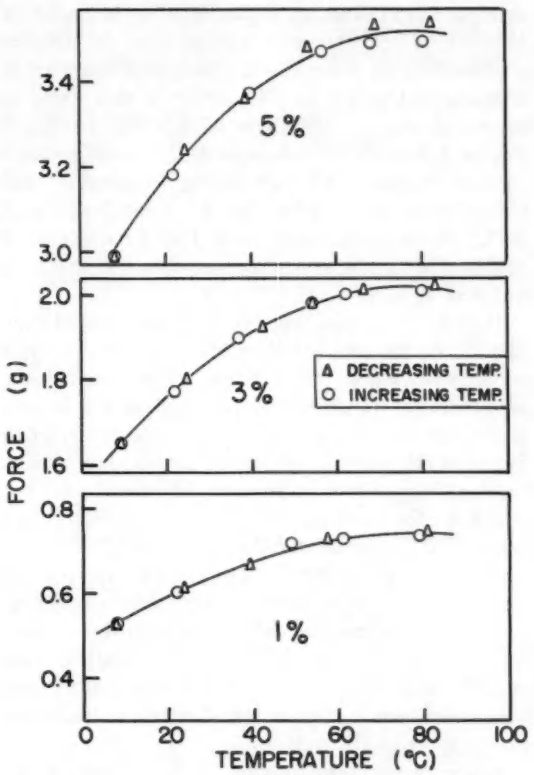

Fig. 3. Force-temperature behavior of textile viscose rayon yarn after swelling with 18% sodium hydroxide without tension.

the transition temperature, an entropy decrease with stretching (rubberlike behavior) is indicated.

The shape of the force-temperature curve for viscose rayon does not appear to be influenced appreciably by the extension of the fiber. The force components at 70°C calculated from equation (5) are shown in Table II. It can be seen that the entropy force component, f_S, is constant for extensions above 1%. The increase in tension with stretching beyond this point must, therefore, be due to the action of energy forces.

If water-fiber interactions, rather than configurational entropy changes, were responsible for the observed force-temperature behavior, a change in sign of the partial derivative $(\partial n_1/\partial T)_{l,P}$ in equation (6) should occur at 45°C for viscose rayon in water. This predication could be confirmed by regain-temperature studies at high humidities in the temperature range indicated. Such measurements would be quite helpful in deciding the correct interpretation of the present results.

Alkali-Swollen Viscose Rayon

Approximately 25-cm lengths of 150-den viscose rayon multifilament yarn were knotted at each end and swollen in concentrated caustic solution without tension. The procedure followed was: (1) to wet out the filaments thoroughly in 0.005% aqueous Ultrawet 30 DS solution; (2) to soak them 10 min in 18% sodium hydroxide; and (3) to wash until neutral with 0.5% acetic acid, followed by water. After neutralization and washing, the yarn was allowed to dry under room conditions before force-temperature measurements were made. (Considerable shrinkage and loss of orientation occurred during this treatment. Some low-molecular-weight cellulose would be expected to be washed out of the filaments under these conditions.)

The observed force-temperature behavior of alkali-swollen viscose rayon at extensions up to 5% is illustrated in Figure 3. Similar results were found

at higher extensions up to the breaking extension of about 35%. The results indicate that the swollen viscose yarn in water has a rubberlike character at temperatures as low as 5°C, similar to that found in untreated viscose only above 45°C. The results in Figure 3 show that the slope of the force-temperature relation decreases with increasing temperature and either levels off or passes through a maximum near 80°C. A force maximum would indicate a transition comparable to that which has been found in undrawn nylon at 40°C [4].

If there is a minimum in the force-temperature relation of the alkali-swollen viscose rayon, it must occur well below 0°C. Such a lowering of the second-order transition temperature would be expected due to the weakening of interchain attractive forces in the amorphous regions which accompanies the swelling. Thus Roseveare [13] found that the transition for isotropic viscose rayon in water was below 5°C, whereas for highly oriented Fiber G rayon it was above 90°C. The fact that the present results fall into the general pattern for orientation-dependence of the transition temperature suggests that molecular configuration changes, rather than possible changes in the swelling-temperature behavior, are responsible for the shift in the transition region upon alkali swelling.

Elastic force constants at 25°C calculated for caustic-swollen viscose rayon are shown in Table III. Comparison with Table II reveals that the entropy force is much more important after the swelling treatment. Furthermore, the entropy of the swollen rayon-water system decreases with increasing extension up to the breaking point, whereas in untreated viscose rayon all the entropy decrease occurs within the first few per cent of elongation. The cellulose network in the swollen viscose rayon thus is much more like the network of chains in rubber than that of the untreated rayon.

At low extensions, the energy force component for highly swollen rayon is negative. This effect has been previously noted for casein [19], acetylated casein [8], and nylon [4], and is probably due to an increase in the attractive forces between chains which occurs as the specimen is stretched.

TABLE III. Force Components of Alkali-Swollen Viscose Rayon Yarn in Water at 25°C

Yarn denier = 150 before treatment

Extension (%)	f_{total} (g)	f_S (g)	f_E (g)
1	0.61	1.43	−0.82
3	1.80	2.42	−0.62
5	3.23	3.31	−0.08
10	6.53	4.29	2.24
15	9.69	5.42	4.27
25	15.73	6.11	9.62

Cotton

Measurements on single cotton fibers were unsuccessful because of the very small forces and force changes involved, and because the short length of the fibers served to magnify thermal expansion and load cell deflection errors. Tests were, therefore, made on a combed cotton 36's yarn of twist multiple 3.80, spun for the Textile Research Institute Cotton Research Project from Deltapine 15 cotton. In interpreting the results, the assumption is made that the only temperature-dependent force acting on the yarn after the initial stress relaxation is due to tension on individual fibers.

The force-temperature behavior recorded for this cotton yarn is depicted in Figure 4. Glasslike elasticity was observed over the entire range of temperature. However, the shape of the force-temperature relation suggests that there may be a transition to rubberlike elasticity near 100°C, comparable to the transition in viscose rayon at 45°C. This feature indicates that there is greater restriction on molecular motion in the amorphous regions of cotton fibers than in the case of viscose rayon, and that a higher temperature is required to attain the freedom of motion associated with rubberlike elasticity.

Under the assumption that thermal expansion is responsible for the force change with temperature, the stiffness of the relaxed yarn measured at a given extension and temperature, along with the force-temperature coefficient under the same conditions, permits calculation of the linear coefficient of expansion by the relation

$$\alpha \equiv \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_{f,P} = -\left(\frac{\partial f}{\partial T}\right)_{l,P} \Big/ l\left(\frac{\partial f}{\partial l}\right)_{T,P} \quad (9)$$

Stiffness values were measured by means of a small incremental extension of the yarn after completion of the force-temperature cycle. At 1 and 5% extension, values of 0.52×10^{-5} and 0.59×10^{-5} per °C were calculated for the linear coefficient of expansion, α. These are well below the value of 1.7×10^{-5} reported by Andersen [1] from stress-strain

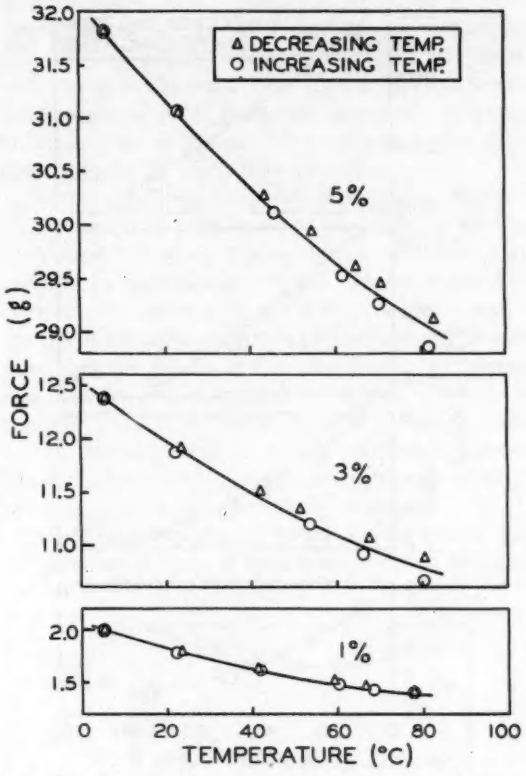

Fig. 4. Force-temperature behavior of 36's combed cotton 148-den yarn.

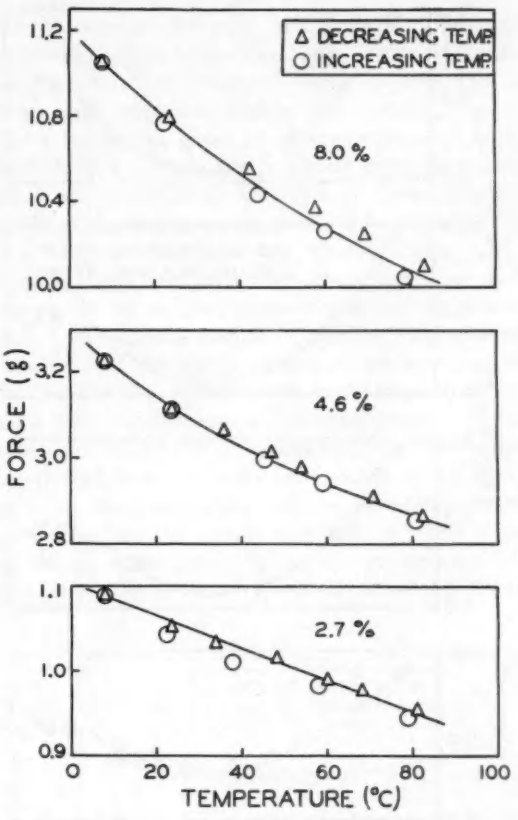

Fig. 5. Force-temperature behavior of combed cotton yarn after mercerization with 18% sodium hydroxide without tension.

measurements on cotton fibers at two temperatures. Andersen's values would be expected to be too large if permanent set occurred during his successive streaching of fibers at two temperatures. On the other hand, the present values would be too low if fiber slippage occurred during the stiffness measurements, or if there were rubberlike elastic elements in the fiber obscured by the overall glasslike elasticity.

Mercerized Cotton

The force-temperature results shown in Figure 5 were obtained after mercerization of the above-mentioned cotton yarn by the swelling procedure employed with viscose rayon. It can be seen that the same general type of elasticity is found both before and after mercerization. This result is in sharp contrast with the marked change in elastic behavior produced by similar treatment of viscose rayon. The strength of intermolecular attractions in the amorphous regions of mercerized cotton, while undoubtedly lower than in the original yarn, still appears to be greater than in untreated viscose rayon.

Experimental Cellulose Acetate and Saponified Acetate

In order to study the effect of acetate side groups on elastic behavior, an experimental cellulose acetate multifilament yarn and the regenerated cellulose yarn obtained by saponification of the acetate under tension were studied. Both of these fibers were of relatively high orientation, as indicated by X-ray diffraction results [3].

In this test a small number of experimental acetate fibers were mounted in parallel. Breakage occurred in the hot water near 6% extension, indicating that the fibers were highly oriented. A transition from

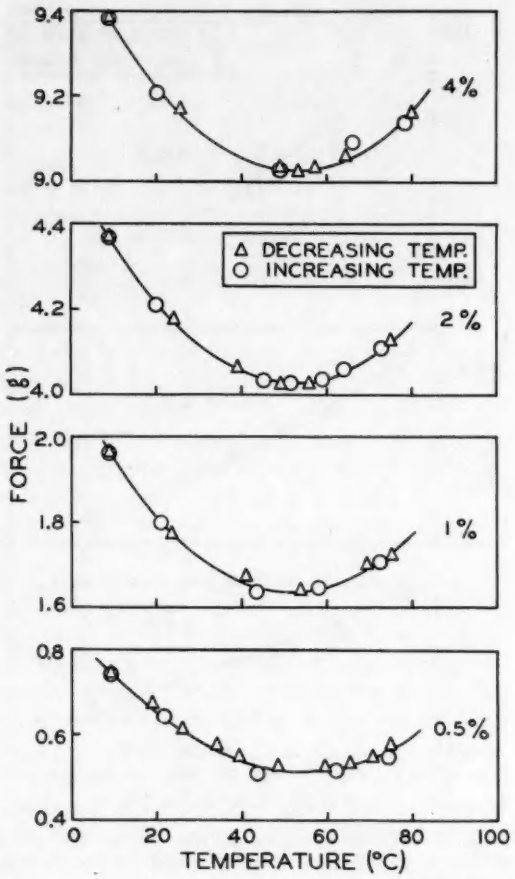

Fig. 6. Force-temperature behavior of highly oriented experimental cellulose acetate filaments.

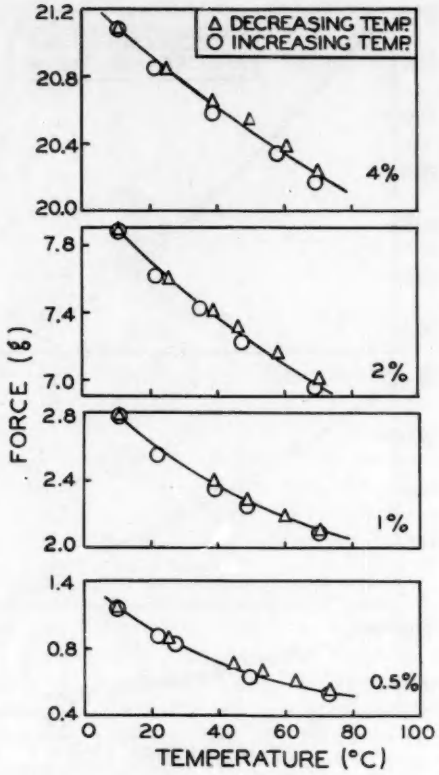

Fig. 7. Force-temperature behavior of highly oriented regenerated cellulose (approximately 15 den) obtained by saponification under tension of the experimental acetate of Figure 6.

glasslike to rubberlike elasticity was observed to occur at about 50°C (see Figure 6). This result indicates that the molecular chains in the amorphous regions of the highly oriented acetate in water have about the same freedom of motion as those in viscose rayon under the same conditions. The greater orientation in the experimental acetate apparently compensates for the weaker interchain attractions.

The highly oriented saponified acetate sample showed the force-temperature behavior indicated in Figure 7. As in the case of cotton, glasslike elasticity was found over the entire temperature range. The chemical structures of cotton and the regenerated fiber are, of course, the same, and the present results indicate that molecular motions in the amorphous regions of the two fibers are about equally restricted. The linear coefficient of expansion calculated from equation (9) ranges from 0.6×10^{-5} to 0.8×10^{-5}/°C, in good agreement with the values of about 0.6×10^{-5}/°C obtained on cotton. A comparison of Figures 6 and 7 shows that acetylation of cellulose hydroxyl groups has the effect of lowering the temperature of transition from glasslike to rubberlike behavior, i.e., there is less restriction on molecular motions in the amorphous regions of the acetate.

Commercial Cellulose Acetate

Measurements were also made on two commercial-type textile cellulose acetate samples. One of these was a 75-den multifilament yarn spun by Celanese only 3 months before testing. The other was a 25-den monofil spun by Tennessee Eastman Corporation in 1949 five years before testing. Both samples were

of considerably lower orientation than the experimental acetate sample described in the preceding section. As a result, both yarns exhibited very large force decay due to stress relaxation at the maximum temperature of 80°C before an essentially constant force could be obtained. This relaxation was particularly great at the higher extensions.

Force-temperature behaviors of these two commercial acetate yarns were found to be similar, indicating no pronounced effects due to aging or differences in methods of manufacture. (See Figures 8 and 9.) At the lower extensions, the curves exhibit a negative force-temperature coefficient with some indications that the curves at the very lowest extensions and minimum temperatures even pass through a maximum. At the very highest extensions, the force-temperature curves exhibit minima similar to those observed for the highly oriented experimental cellulose acetate yarn previously described.

A tentative explanation of these observations can be made on the basis of known stress-strain behavior of cellulose acetate filaments and the force-temperature observations for other textile fibers. Commercial, essentially unoriented cellulose acetate filaments exhibit a stress-strain curve which involves first a short elastic region of high elastic modulus, then a plastic region of great extension with very little increase in force, and finally a short region in which the curve swings in the direction of higher stresses as the reorientation in the plastic flow region gives rise to reinforcement of the fiber structure [20]. Because there is considerable stress relaxation and flow occurring in the filament before force-temperature measurements can be made, the filaments as measured for the higher extensions are more apt to behave like the well-oriented experimental acetate yarn than the filaments at lower extension. These latter are in process of changing from the initial unoriented structure to the final more oriented state. It is not surprising, then, that the force-temperature curves fall into two groups exhibiting different types of behavior, one group for extensions between 1.0 and 5.0%, the other for extensions exceeding 20%.

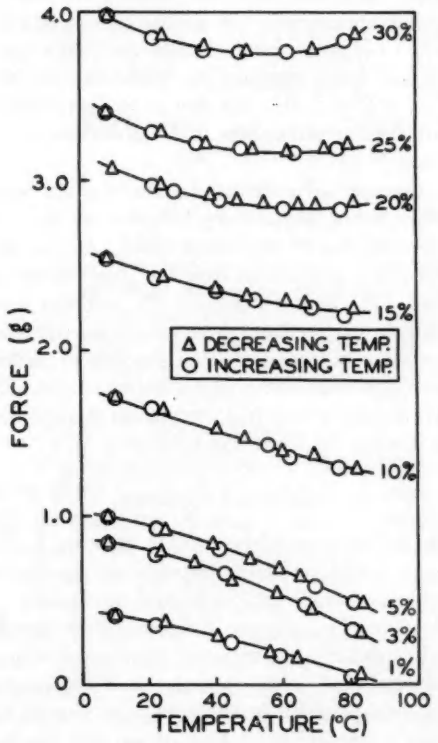

Fig. 8. Force-temperature behavior of 3-month-old commercial-type cellulose acetate, 75-den yarn.

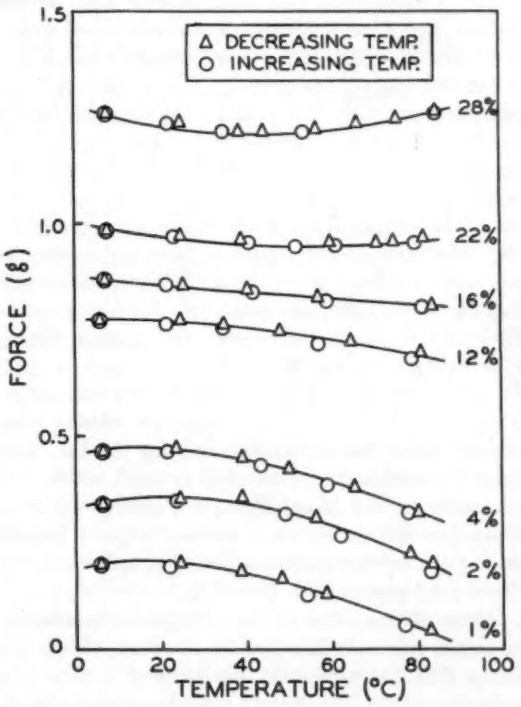

Fig. 9. Force-temperature behavior of 5-year-old commercial-type cellulose acetate, 25-den filament.

At the lowest extensions and temperatures, the maximum in the force-temperature curve suggests that, as a result of rearrangements which are occurring in the filament, the forces between the cellulose acetate chains are increasing and the motions of the chains are being restricted. This restriction of motion may be somewhat similar to crystallization in the sense that now the chains are condensed or organized into a structure which responds to external forces as a unit. (This phenomenon need not correspond to crystallization in the X-ray sense.) The formation of these units under stress will lead to a reduction in the force acting on the fiber. Similar phenomena have been observed in nylon fibers [4]. This picture of the changes taking place in the cellulose acetate fiber is supported by the fact that in the experiment the force initially underwent a rapid increase followed by a slow decrease to an equilibrium value after the temperature was reduced rapidly to its lowest point (about 5°C). When the temperature was increased from this point, a momentary decrease in force followed by a gradual increase was observed. The time dependency of force under these circumstances is similar to that observed for rubber under conditions of temperature and extension where crystallization is known to occur [5].

At the high extensions the commercial cellulose acetate filament differs from the highly oriented filaments previously described in that the transition temperature between glasslike and rubberlike behavior appears to depend somewhat on the extension; the greater the stretch on the fiber, the lower the transition temperature. The intermolecular forces restricting motions, probably in the amorphous regions of the fiber, are apparently decreasing as the fiber is stretched to a greater and greater extent. One explanation for this observation might be that, in order for the orientation of the amorphous regions to occur during the elongation of the fiber, certain molecular structures existing in the fiber must be broken up. This process need not involve crystallites in the X-ray sense. It may merely be a disappearance of the local ordered regions formed during the rearrangements already postulated at the lower extensions of the fiber.

These observations of force-temperature behavior of commercial cellulose acetate filaments clearly indicate that the structural mechanisms involved in extension of the filament are indeed complex, changing in nature and extent as the fiber is stretched to its breaking point.

Conclusions

1. Force-temperature measurements can be used to classify the elastic behavior of cellulose fibers in water as either glasslike (energy forces predominant) or rubberlike (entropy forces predominant). Water-fiber interactions may have an influence on the interpretation of the results, but further experiments on the swelling and sorption behavior of cellulose fibers in water are needed to clarify this point.

2. A transition in the elastic behavior of textile viscose rayon in water occurs at about 45°C, with partial rubberlike behavior occurring above and glasslike elasticity occurring below this temperature. At 70°C, all the entropy decrease upon stretching occurs within the first 1 or 2% extension.

3. Alkali swelling increases the rubberlike elasticity of viscose rayon and lowers the temperature of transition from glasslike to rubberlike elasticity.

4. Cotton exhibits glasslike elasticity in water at temperatures from 5° to 80°C. Mercerization does not cause any pronounced increase in the rubberlike character of cotton over this temperature interval.

5. Saponification of the acetate groups in a highly oriented cellulose acetate lowers the temperature of transition from glasslike to rubberlike elastic behavior, indicating that the side groups act to decrease intermolecular attractions and restrictions on chain motions.

6. Commercial cellulose acetate exhibits basically different force-temperature behavior at low extensions from that at high extensions. At low stretch the elasticity is glasslike over the temperature range studied. At high extensions the material behaves like highly oriented cellulose acetate except that the temperature of transition from glasslike to rubberlike elasticity decreases with increasing extension. These behaviors may result from structural changes taking place during the stretching process.

Acknowledgments

The authors are indebted to Dr. Howard J. White, Jr., for making available unpublished equations on the effects of water and for helpful discussions. The courtesy of the Celanese Corporation in supplying experimental and regenerated cellulose acetate and commercial-type acetate samples, and the American Viscose Corporation in supplying the viscose rayon sample, is appreciated. One of us (G. M. B.) is grateful to Textile Research Institute for a fellowship grant which made this work possible.

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The Structure of Resistant Membranes Isolated from Oxidized Wool

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Abstract

Evidence is presented of the nature of the resistant residue obtained from wool oxidized with peracetic acid and extracted with ammonia. The use of gold shadowing and phase contrast in optical microscopy reveals cortical cell membranes, nuclear membranes, nuclear remnants and resistant fibrils derived from the cortex, and the composite nature of the cuticular sheath.

Introduction

The chemical stability of the keratins, which form the bulk of the weight of a wool fiber, is attributed to the high content of cystine, through which numerous intermolecular disulfide bridges are formed. It has been shown that oxidation of these disulfide bridges with aqueous peracetic acid renders the major part of the wool fiber soluble in dilute alkali, but microscopic examination reveals that a system of membranes remains which appears as a "ghost" of the original fiber [1, 2]. As they are not rendered soluble by this treatment it must be concluded that their chemical stability is dependent on chemical linkages other than disulfide bonds. The nature of these linkages is not known at present.

Alexander and Earland, who first isolated these membranes, claimed to have discovered a new histological component in wool located between the cuticle and the cortex. This claim has not been substantiated by subsequent investigators who have shown that the membranes are derived from both cuticle and cortex [6, 10, 14]. Of particular interest are the electron micrographs obtained by Manogue and Moss, which show that cortical cell membranes are present and that they form a continuous network throughout the cortex [9].

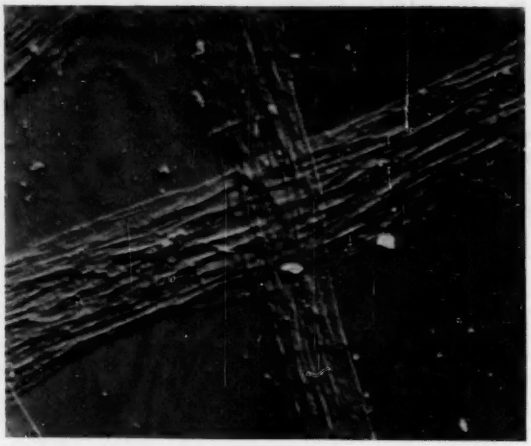

Fig. 1. Resistant membranes isolated from merino 64's quality wool oxidized with peracetic acid and extracted with ammonium hydroxide. Gold shadowed at 35°, positive print, ×230.

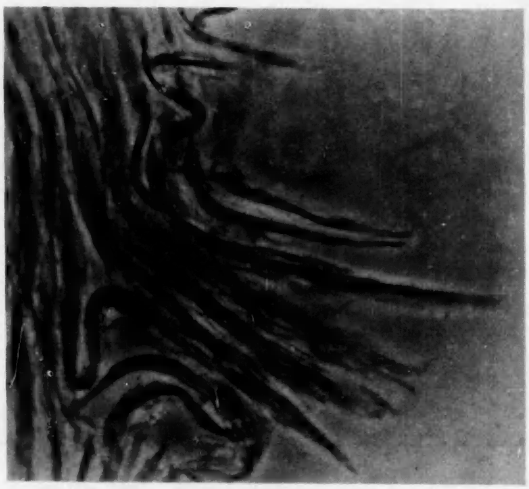

Fig. 3. Resistant material derived from the cortex, showing remnants of cortical cells. Phase contrast ×500.

It is to be expected that the resistant membranes will play an important part in determining the accessibility of the wool fiber to chemical reagents, particularly those of large molecular dimensions. As such, these membranes are likely to be a major factor in determining the behavior of wool to dyeing and chemical processing. In view of this, it is unfortunate that the use of the optical microscope in the elucidation of structural detail in the membranes is handicapped by their poor visibility due to lack of contrast.

The authors have recently pointed out that the use

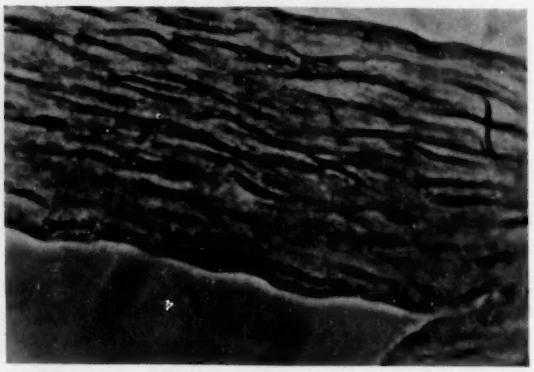

Fig. 2. Resistant material derived from the cortex, showing granular nuclear remnants. Phase contrast, ×500.

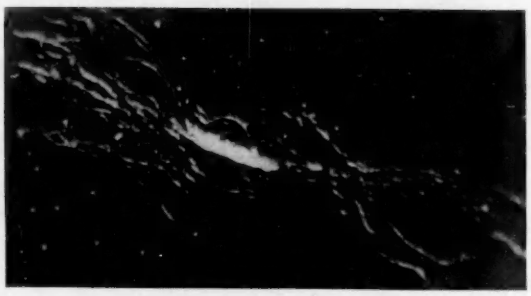

Fig. 4. Resistant fibrils associated with the nuclear remnant of a cortical cell. Gold shadowed, positive print, ×1000.

Fig. 5. Resistant fibrils and nuclear remnant derived from a cortical cell. Gold shadowed, negative print, ×1000.

of gold shadowing in optical microscopy reveals a wealth of detail in structures of this type [4] and have examined the resistant membranes by this method, supplementing this observation by the use of phase contrast.

Preparation of Resistant Membranes

Selected samples of solvent-scoured merino 64's quality wool were oxidized with 1.6% peracetic acid

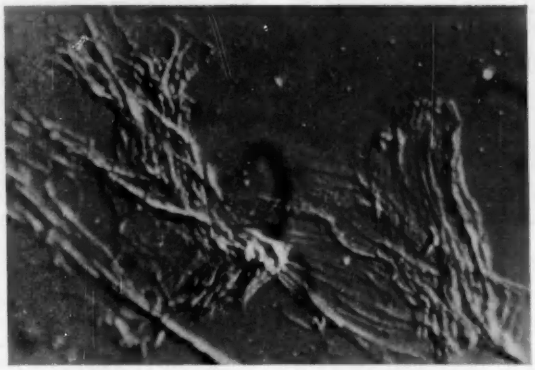

Fig. 6. Resistant fibrils and cortical cell membrane. Gold shadowed, negative print, ×1350.

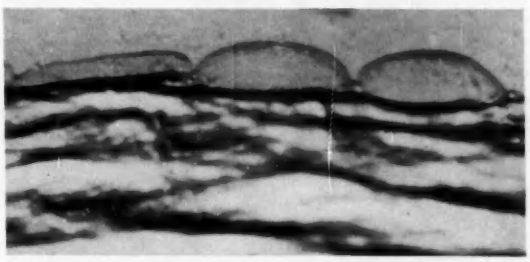

Fig. 7 and 8. Folds of epicuticle which are attached to the resistant cuticular sheath near the scale tips, but otherwise detached. Gold shadowed, positive prints, ×1500.

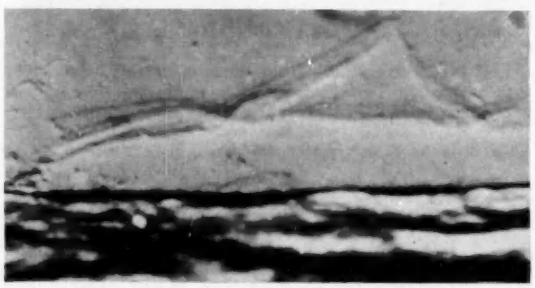

Fig. 9. A sheet of epicuticle that is completely detached from the cuticular sheath. Gold shadowed, positive print, ×1500.

Fig. 10. A sheet of epicuticle covers the field and is attached in one area to a cuticular sheath remnant. Streaks of adhering protein mark the points of attachment to the cuticular sheath. Gold shadowed, positive print, ×1000.

for 24 hr, thoroughly washed in distilled water, and dried. The oxidized wool was treated with 1 *N* NH_4OH, and the insoluble material was isolated by centrifugation. This was repeated five times with a final rinse in distilled water.

The resistant membranes were then gently abraded in water between microscope slides, dried down, and shadowed with gold at an angle of 35° in the manner described elsewhere [4]. Examples of the structures observed are shown in Figures 1, 4–11, and 14–16, and Figures 2, 3, 12, and 13 were obtained using phase contrast with unshadowed specimens.

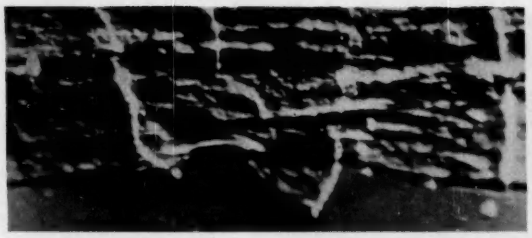

Fig. 11. An example of the membranous flaps which lie beneath the epicuticle in the cuticular sheath. Gold shadowed, positive print, ×1350.

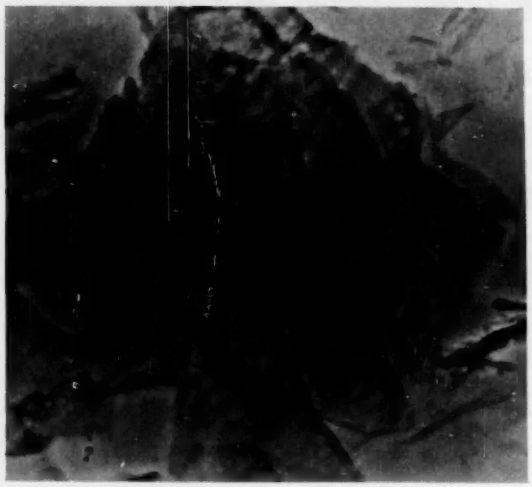

Fig. 13. Part of a cuticular sheath showing doubling of scale pattern due to epicuticle folds, and cuticular sheath after detachment of epicuticle (*C*). Phase contrast, ×1000.

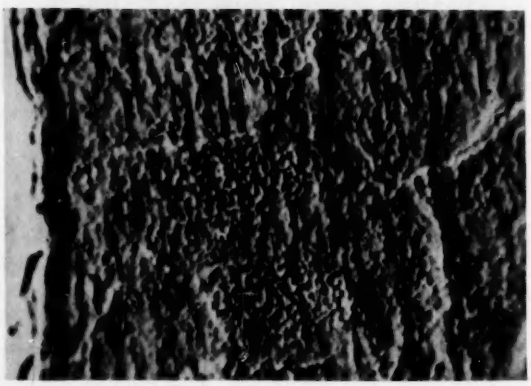

Fig. 15. The texture of the inner surface of a thicker part of a cuticular sheath showing pitting of inner surface. Gold shadowed, negative print, ×1350.

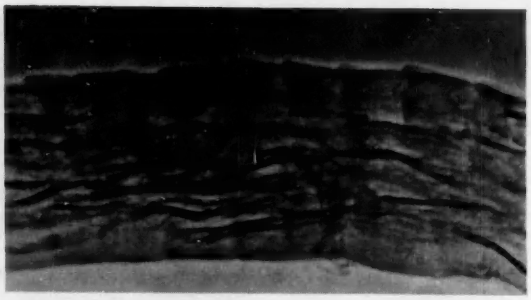

Fig. 12. General view of resistant material showing cuticular sheath thickened near scale tips, a membranous flap marked *M*, folds of detached epicuticle, and nuclear remnants. Phase contrast, ×500.

Fig. 14. The texture of the inner surface of the cuticular sheath showing continuous fibrillar layer and membranous flaps along folded edge (*M*). Gold shadowed, positive print, ×1200.

Structural Detail

The intact membranes (Figure 1) appear as thin flattened tubes with a surface texture which is reminiscent of both the scale pattern of the cuticle and the elongated cortical cells. The shadow casting has emphasized each feature separately according to the direction of the incident metal relative to the fiber axis. The extreme thinness of the tubes may be appreciated from an examination of the area of the photograph in which they cross. Apart from the texture mentioned, the external surface appears smooth, suggesting that the epicuticle remains intact, thereby masking the underlying structures.

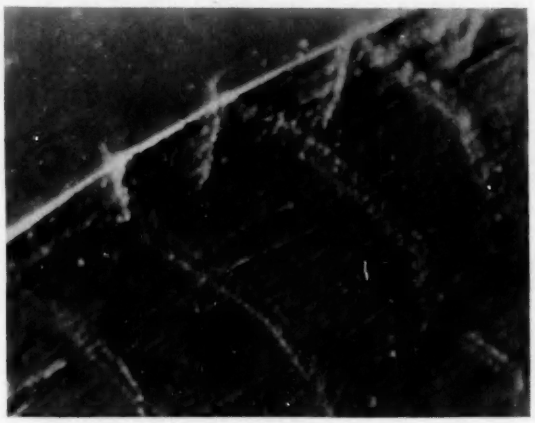

Fig. 16. Inner surface of cuticular sheath showing continuous fibrillar layer and doubling of scale pattern due to underlying folds of epicuticle. Gold shadowed, positive print, ×1200.

The rupture of the outer tube releases the resistant components derived from the cortex, and some features of these are shown in Figures 2–6. The major part of the cortical cells has dissolved, but the nuclear remnants are markedly resistant to the chemical treatment. The granular nature of the contents of the nuclear space is clearly visible in Figures 2 and 3, obtained by using phase contrast. Gold-shadowed preparations reveal a system of resistant fibrils associated with the nuclear remnant as in Figures 4 and 5, and these probably correspond to the intracellular remnants noted by Mercer [11] and also by Manogue and Moss [9] in cross sections of wool fibers oxidized with peracetic acid and treated with alkali.

The cortical cell membranes observed by Manogue and Moss [9] in the electron microscope were of the order of 100 Å in thickness; they are, however, also visible in the optical microscope in the gold-shadowed preparations, and an example is seen in Figure 5 where a wrinkled membrane lies alongside a group of resistant fibrils. Little detail can be seen in the membranes, but there is a suggestion of the pleated surface visible in the electron microscope [11].

The resistant fibrils and the nuclear remnant appear to be closely associated, as they are rarely separated during the mechanical disruption of the wool treated with peracetic acid-ammonia. The cortical cell membranes, however, generally occur in irregular fragments distinct from the resistant fibrils and nuclear remnants. It is unlikely, therefore, that these fibrils correspond to those which adhere to the cortical cell membranes in the manner described by Manogue and Moss [9].

The nature of the resistant component of the cuticle is more difficult to ascertain. Mercer [11] has described it as the external layer of the cuticle, or cuticular sheath, and Manogue and Elliott [8] give an essentially similar description. It is at once apparent from Figures 7 to 16 that resistant residues of many histological components of the cuticle are present.

The simplest component to identify is the epicuticle, which appears to be detached from the fiber except at the scale junctions. This feature is illustrated in Figures 7, 8, and 12. Sheets of epicuticle which are completely detached from the fiber are commonly observed, as in Figures 9 and 10. The ridges of adhering material marking the line of attachment to the scale junctions are particularly clear in Figure 10.

Beneath the epicuticle there appears to be a system of somewhat thicker overlapping membranes, which are frequently seen to lift away from the main part of the cuticular sheath, as in Figures 11 and 12. The disposition of these membranes in the cuticle is not immediately apparent and will be discussed later. Both phase-contrast and gold-shadowed preparations indicate that these flaps are thickened towards the tip edge and that the folded edge of the epicuticle is displaced from them towards the tip of the fiber. Figures 7, 12, and 13 illustrate this feature. The inner surface of the cuticular sheath seen in Figure 14 is essentially fibrillar. The transverse ridges appear to be caused by the underlying membranous flaps since the contours can be followed across the folded edge. The fibrillar material is continuous across the ridges both in Figures 14 and 16.

The effect of the peracetic acid-ammonia treatment on the inner layers of the cuticle is variable. In some cases a thicker cuticular sheath is obtained, as in Figure 15, which shows a number of interesting features. The transverse ridges in this case are more likely to be due to the inner scale edges which are now known to project from the general level of the inner surface of the cuticle [5]. The inner surface of these thicker cuticular sheaths is pitted, and the pitting is more pronounced near the inner scale edges.

In other cases the cuticular sheaths are thinner than that of Figure 14, and the transverse ridges are doubled. The displacement of the folded edge of the

underlying epicuticle from the tip of the membranous flaps, seen so clearly in Figure 13, probably accounts for the second ridge.

Discussion

The general impression gained from the gold-shadowed prepartions is confirmation that residues of many histological components are present in the residue from wool after peracetic-ammonia extraction, and no evidence to support the claim that the residue constitutes a subcuticular membrane was found. The nature of the "various minor components appearing as particles or rodlets within the cortical cells" noted by Mercer [11] is now clear. They consist of fibrils, which are of a similar diameter to those released by the action of trypsin, and an essentially intact nuclear remnant containing dense material originally derived from the nucleoproteins of the developing cells.

The marked difference between the appearance of the nuclear remnant in phase contrast, where it is seen to be granular, and that of gold-shadowed specimens, where it is featureless, strongly suggest that the nuclear space is surrounded by a resistant membrane. Further support for the presence of a membrane is the fact that the granules, which appear quite distinct in phase contrast, do not disperse. This resistant membrane around the nuclear remnant is presumably derived from the original nuclear membrane of the developing cell.

The lengths of the resistant fibrils are a significant fraction of the length of a cortical cell, and they are closely associated with the nuclear remnant. They show no tendency to adhere to the cortical cell membranes and therefore are probably distributed throughout the volume of the cortical cell. The reason for the resistance of the fibrils, which represent only a small fraction of the original cell volume, is not known. Both their chemical resistance and close association with the nucleus, however, are probably related to the sequence of events in the follicle occurring during the differentiation of the cortex, for Auber [3] has shown that the differentiation of fibrils in the presumptive cortical cells commences around the nucleus.

The variable nature of the cuticular sheath renders interpretation more difficult than with the residues derived from the cortex. The thicker sheaths of the type seen in Figure 15 appear morphologically to consist of the entire cuticle in which the release of the oxidized keratin is only incipient. The pits which appear on the inner surface probably mark areas where the bulk of the endocuticle has been removed. It is interesting to note the increased pitting towards the inner scale edges.

The frequent occurrence of epicuticle in preparations of the type that we have examined has already been noted [6, 8, 11]. The relation between the epicuticle and the underlying layers is, however, not established, and Figures 7, 8, 10, 12, and 13 throw considerable light on this point. The epicuticle appears completely detached from the fiber except along lines near the scale edges. These lines are marked in isolated epicuticle by adhering protein, as in Figure 10. From Figures 7, 8, and 12 the epicuticle appears to be tucked in beneath the edges of the membranous flaps mentioned previously, and when they are raised the epicuticle adheres to the flap rather than to the underlying fibrillar material. It seems likely, therefore, that the thickened edges seen in phase contrast correspond to the point of attachment of the epicuticle beneath the edges of the membranous flaps.

The frequent parallelism of the folded edge of the epicuticle to the edge of the membranous flaps strongly suggests that the tips of the scales have been dissolved away. However, considerable swelling occurs when the oxidized fibers are treated with alkali, and this together with possible osmotic effects within the cuticle itself may distort the morphology of the resistant components.

The relation of the remainder of the cuticular sheaths to the fine histology of the intact cuticle is difficult to visualize. Evidence that we have obtained from gold-shadowed preparations of wool fibers treated with a variety of chemical reagents and enzymes [5] suggests that the structure of the cuticle is more complex than is generally believed [7]. A preliminary interpretation of the cuticular sheath will be offered, however, in the nomenclature employed by Lindberg *et al.* [7] pending further investigation of the fine structure of the cuticle.

The relation between the membranous flaps and the epicuticle previously discussed suggests that the exocuticle has been completely lysed and it is logical therefore to regard the membranous flaps as lying between the exocuticle and endocuticle. Some support for this view is obtained in gold-shadowed preparations of trypsin-degraded cuticle (Figure 17), where the outer layer of the enzyme-resistant endocuticle is found to be smooth and featuresless with

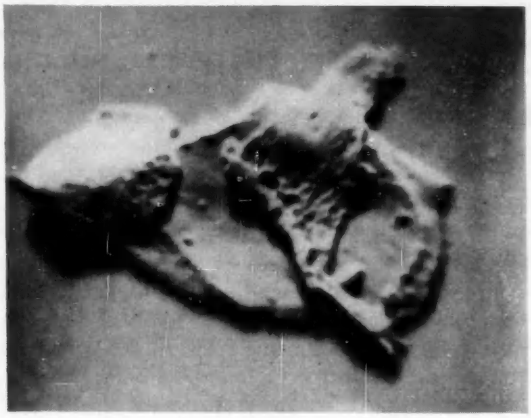

Fig. 17. Scale fragment from wool partially digested with crude trypsin. The smooth outer surface is to be contrasted with the furrowed inner surface of the overlying fragment near the center of the photograph. Gold shadowed, negative print, ×2000.

ridges which follow a characteristic scale pattern. The generally accepted view of the nature of the endocuticle is seen in the furrowed inner surface of the scale fragment which lies on top of the main fragment. The fibrillar component of the cuticular sheaths isolated by peracetic-ammonia extraction, which is continuous, probably represents the outermost layer of the endocuticle, and this feature is depicted diagrammatically in Figure 18.

A Note on the Allwörden Reaction in Oxidized Fibers

Mercer and Golden [12] have claimed that an Allwörden reaction may be produced in oxidized wool by the addition of 1% sodium bicarbonate solution, and cite the coalescence of the bubbles as evidence for a continuous epicuticle. Parisot and Leveau [13] have criticized this claim but do not mention any repetition of the reaction. The authors have attempted to produce the reaction in a variety of wools and hair, varying the experimental conditions over wide limits, but have been unable to repeat the observation. They feel, therefore, that the appearance or nonappearance of bubbles must be a function of the particular wool sample chosen and the individual technique of the experimenter. Whether the reaction recorded by Mercer and Golden is accepted as a general property of oxidized wool must await further investigation.

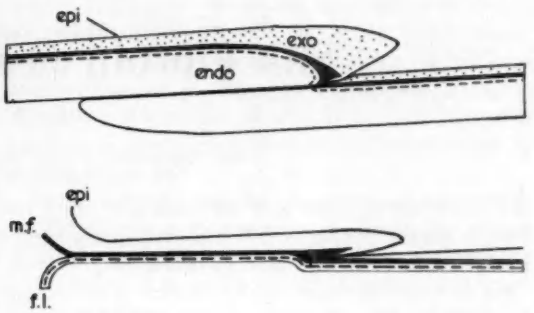

Fig. 18. A possible derivation of the components of the resistant cuticular sheath. *Top*, their location in the intact cuticle; *epi*, epicuticle; *exo*, exocuticle; *endo*, endocuticle. *Bottom*, the composition of the cuticular sheath; *epi*, epicuticle, *m.f.*, membranous flap, *f.l.*, continuous fibrillar layer.

The authors are in agreement with Parisot and Leveau that the membrane limiting the bubbles in Figure 1 of Mercer and Golden's paper cannot be epicuticle; this is clear from the optical cross section. It probably corresponds more nearly to a thickened cuticular sheath similar to that shown in Figure 15, which is readily detached from the resistant components of the cortex by mild mechanical abrasion.

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Silk Fibroin as a Fibrous Protein[1]

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IT IS probably true that the past few years has been a period during which chemical developments in the textile field have been of outstanding interest. This is especially true of the fibrous proteins, our knowledge of the detailed constitution and structure of which has considerably advanced during the past decade. Today, the natural fibers that have been used by man for several thousands of years have been significantly replaced, or perhaps it would be more correct to say supplemented, by regenerated and synthetic fibers. The evolution and development of these synthetic fibers, however, have undoubtedly been initiated and stimulated by the vast background of knowledge that has arisen from studies of the natural fibers. The classic researches of Fischer and Abderhalden, who demonstrated the chainlike structure of the protein molecule, marked the beginning, and the elegant researches of Carothers on the synthesis of macromolecules denoted the end, of what might be described as the first phase in synthetic fiber production.

In this half century of development, man has often turned to the natural product for guidance and inspiration. Perhaps two natural fibers have provided the main fundamental models of fibrous macromolecular structures; these are cellulose with glucose as the sole building unit and silk fibroin with many of the naturally occurring amino acids linked together to give a more complex chain molecule. The chemist occupied with laboratory synthesis of fibrous polymers must have frequently turned his thoughts to the creation of the delicate filament by the small insignificant caterpillar of *Bombyx mori*. Indeed, the natural formation of fine fibers is worthy of deep consideration for it presents interesting examples of the synthesis of a fiber-forming material that possesses properties which contribute to the ultimate production of fine filaments. Some of these are: The fibrinogen of the blood, a soluble protein that, when acted on by a complex enzyme system, forms a delicate network of fibrils which envelop and retain the blood elements in the form of a clot; the hagfish, *Polistotrema stouti*, which excretes a slime consisting, according to the studies of Ferry [4], mainly of a protein (mitin) that appears to be a globular protein convertible into fine elastic fibrils of approximately 1 μ in diameter; the spider that, in order to catch its prey, constructs a fine web from a gossamer filament that possesses the properties of tenacity and elasticity so valued in textile filaments; the silkworm, that spins its double filament, suitably sized with sericin, in order to construct its habitat for the pupation stage. All these phenomena serve as an object lesson to the chemist concerned with the synthesis and regeneration of filaments not only with regard to the nature of the final product but also in the mechanism by which an initially soluble protein is converted into a strong, insoluble filament.

[1] Presented before the Division of Polymer Chemistry at the annual meeting of the American Chemical Society in New York City on September 16, 1954.

Chemistry

Silk fibroin is a comparatively simple protein, free from sulfur-containing amino acid residues and from amide nitrogen. Its amino acid constitution is now known almost completely and is shown in Table I. The data have been largely obtained by Smith and coworkers at the Shirley Institute, while the values for the basic amino acids, histidine, lysine, and arginine, were recently determined in the laboratories of the Wool Industries Research Association; these latter values, which are considered to be correct to within $\pm 4\%$, are of special significance in relation to the molecular weight, to which further reference will be made. The work of Coleman and Howitt [2] showed that, when fibroin is dissolved in a cupriethylenediamine reagent, the resulting solution neutralized with acetic acid, and the cupriethylenediamine diacetate removed by dialysis, an aqueous solution of fibroin is obtained. When cupriethylenediamine of low concentration is used, the resulting solution gives a mucilaginous precipitate on acidifying to *p*H about 3, whereas the remainder of the protein remains in solution in the water-clear supernatant liquor. Under suitable conditions of solvent concentration and time, practically all the

fibroin can be converted into the water-soluble form that is not coagulated by acidification. Aqueous preparations of the acid-stable, water-soluble protein set to a solid gel after being kept at room temperature for a few days, while precipitation by the normal protein-precipitating agents invariably gives a water-insoluble preparation. When the acid-stable, water-soluble preparation is dried on clean mercury in vacuo over phosphorus pentoxide, a transparent film is obtained. This film is soluble in water and has little tensile strength, but if moistened and stretched it extends to about three times its initial length, acquires considerable tensile strength, and becomes insoluble in water. It is considered that these changes are due to the conversion of a soluble globular protein into an insoluble fibrous form and that they afford an unequivocal demonstration of the phenomenon of denaturation.

Coleman and Howitt found a mean molecular weight for the soluble fibroin of about 33,000 when determined by osmotic-pressure measurements in concentrated urea solutions. Holmes and Smith [5], however, examined the soluble fibroin by ultracentrifugal and diffusion methods and found a molecular weight of 60,000 to 150,000 with an average value of 84,000. These latter results are of interest in relation to the contents in fibroin of the basic amino acids. The values found for histidine, lysine, and arginine correspond to an integral molecular ratio of 2:3:5 and indicate that the minimum molecular weight of fibroin is of the order of 84,000, in agreement with the value advanced by Holmes and Smith. Further, if the mean residue weight of 78, found by Coleman and Howitt, is accepted, then the number of amino acid residues in the molecule is slightly above 1000.

TABLE I. Amino Acid Composition of Silk Fibroin

Amino Acid	Grams of Amino Acid per 100 g of Protein	Grams of Anhydro Residue per 100 g of Protein
Glycine	41.2	31.4
Alanine	33.0	26.3
Serine	16.2	13.4
Threonine	1.57	1.33
Aspartic acid	2.75	2.38
Glutamic acid	2.15	1.89
Tyrosine	11.4	10.3
Valine	3.6	3.05
Phenylalanine	3.36	2.99
Leucine	0.9	0.78
Isoleucine	1.1	0.95
Tryptophane	0.65	0.49
Proline	0.7	0.59
Histidine	0.37	0.33
Lysine	0.54	0.47
Arginine	1.00	0.90
Amide nitrogen	Trace to nil	
Total	120.59	97.55

Short, intensive tryptic hydrolysis of the water-soluble protein yields a product of a molecular weight of 8000 to 10,000 which is free from proline and contains less than 1% tyrosine. Drucker and Smith [3] have shown that this product, which is insoluble in water, has a molecular weight of approximately 7000 and consists entirely of glycine, alanine, and serine.

Thus the greater part of the protein chain of the fibroin molecule consists of glycine and alanine residues interspaced with serine and possibly other amino acid residues. This structural unit is supported by the work of Levy and Slobodian [7], who have shown, by means of isotope-derivative methods, that the minimum repeating unit is —glycyl—X_1—alanylglycyl—X_2—, where X_1 and X_2 represent any amino acid other than glycine or alanine.

The more recent work of Kay and Schroeder [6] is substantially in agreement with that of Levy and Slobodian and indicates the main trend of the sequential units of glycine and alanine residues; an extension of this work will doubtless provide important data on the sequence of the tyrosine and proline residues. It is also probable that the amino acid residues with bulky side chains, such as tyrosine, are grouped together in regions that are widely separated along the protein chain. It is of interest, therefore, to focus attention on both the micro- and the macrostructure of the molecule.

Micro- and Macrostructure

The microstructure has been recently and intensively examined by means of X-ray diagrams and infrared spectra. At a recent discussion on the structure and properties of synthetic polypeptides and silk proteins held by the Faraday Society, Warwicker stated that the X-ray diagrams of fibroin from the larvae of *Bombyx mori* show that the structure is based on an orthorhombic unit cell in which are packed antiparallel pleated sheets of polypeptide chains related to one another by a twofold screw axis; Riley and Arndt stated that their X-ray investigations indicated that the unit of structure is

the antiparallel chain pleated sheet of Pauling and Corey. At the same meeting, Kratky reported that the gels formed by the spontaneous coagulation of renatured silk contained rodlike particles several thousand angstrom units in length, and either of square cross section with side 76 Å units or circular cross section of diameter 80 Å units; a low-angle X-ray study also indicated a periodicity of 75 Å units, with one of 100 Å units which was not always reproducible. In general, the X-ray and infrared studies recently carried out lend support to the applicability of the α-helix structure of Pauling and Corey for fibroin. It is clear, however, that the microstructure of the molecular chain in silk fibroin and related synthetic polypeptides, as based on available X-ray and infrared data, requires some clarification. In this connection, Ambrose and coworkers [1] prepared water-soluble fibroin by dissolving silk in dichloroacetic acid or in concentrated lithium bromide solutions. These preparations yielded water-soluble fibroin in sheet form for which infrared spectroscopy indicated the α configuration. This question of the applicability of α and β configurations to fibroin has not been clearly demonstrated. It can be contended that denaturation is basically independent of the α–β transformation.

With regard to the macrostructure of fibroin and to the related phenomenon of denaturation, Coleman and Howitt concluded that the water-soluble or globular form of the protein consisted of a three-limbed folded form in which a molecular hinge was formed by two proline residues at each fold. In the light of recent determinations of the molecular weight, this theory requires at least quantitative adjustment. There is little doubt, however, that the preponderant glycylalanyl regions of the chain readily fit into a lattice to give the crystalline portions of the fiber. The hydrophilic character of the globular form is due to the seryl alcoholic and other polar groups.

The theory of macrofolding, as the fundamental basis of denaturation, raises many points of interest. Thus, the folding and unfolding mechanism in relation to chain structure cannot be considered to apply to keratins and, for these proteins, it must be postulated that denaturation occurs in vivo as an integral and final part of the protein synthesis; the little evidence available points to a water-soluble precursor with sulfur in the thiol form which is oxidized to the insoluble keratin at the site of deposition after appropriate configurational modification of the molecular chains. In this connection, it is of interest to note that the presence of redox mechanisms has been claimed for the blood thrombase system and for the enzyme system present in the larvae of the clothes moth. These phenomena lend support to the conception of a denaturase, an enzyme that brings about denaturation; in this connection, it is not yet clear whether the silk-gland fibroin is denatured mechanically during extrusion by the silkworm or whether the secretion of the glands of Filippi effect denaturation enzymically.

The apparent fission of dithio bonds becomes of importance in a consideration of the conversion of the globular form of insulin into a fibrous material. Waugh and coworkers achieved this conversion by heating to 100° crystalline insulin in solution at *p*H 2–2.5; the fibrous material could be reconverted into the crystalline insulin with crystal habits and physiological activity identical with those of the initial insulin preparation. These changes in the insulin protein are difficult to understand if it is assumed that the processes of denaturation and renaturation are associated with a marked rearrangement of the molecule chain, necessitating fission and reunion of dithio bonds. Recent work by Sanger, however, has indicated that the dithio bonds of insulin are, at least partly, intramolecular (as in lysozyme) and not intermolecular (as in keratin); hence the rupture of dithio bonds is not essential to insulin denaturation.

The folding and unfolding of silk fibroin is uncomplicated by covalent bonds or, probably, by formation of salt linkages. It should be noted, however, that silk filaments, exposed under certain conditions to light irradiation or reaction with some chemical reagents, become insoluble in cupriethylenediamine, and it can be assumed that, in these filaments, the formation of crosslinkages, possibly of the ether type (e.g., from the tyrosine residue), has occurred.

The picture that we therefore have of the silk filament is one in which a very large number of protein chains, each chain consisting of some 1000 or so amino acid residues, are arranged side by side so as to form crystalline regions in which the neighboring chains are linked by hydrogen bonding and of amorphous regions where the amino acid residues with bulky side chains create disalignment, or where, as must happen to a large degree, the alignment of the alanylglycyl units is incomplete. It is possible, of course, that secondary valencies, e.g., van der Waals forces, can operate in addition to hydrogen

bonding, but it is probable that hydrogen bonding is the principal mechanism by which the adjacent peptide chains are interlinked. In this connection, it is of interest to note that, with adjacent alanylglycyl chains, the density of hydrogen bonding is approximately three times that possible in chains of type 66 nylon. Hydrogen bonding undoubtedly plays a major part in the tensile behavior of the silk filament. In some commercial silks, the formation of fibrils, leading to lousiness, is observed. This occurrence is probably associated with a tendency for the molecular chains to form limited aggregates. It was observed that the spinning of fibroin solutions (using cuprietylenediamine solutions and spinning through a single jet into an acid bath) sometimes yielded a filament showing spontaneous fibrillation during the regeneration in the acid bath.

The mechanism by which the long chains can be folded into a more compact form, representing the globular protein, depends, according to Coleman and Howitt, on the presence of proline residues which afford a means of bending the chain through approximately a right angle. Such a theory raises the extremely interesting question as to the role played by the various amino acid residues present in the fibroin molecule. Most biological workers would subscribe to the theory that the protein molecule is a definite molecule made up of a certain fixed number of various amino acids arranged in a definite way. Such a postulate would be supported by the findings of Sanger with regard to insulin. A sequitur of this postulate would be that each amino acid has a definite function in the structure and behavior of the protein molecule. It can be readily assumed that, as described above, the glycine and alanine residues are present to contribute to the hydrogen bonding between the molecules and thus give tensile strength to the aggregate of protein molecules forming the silk filament. Amino acid residues that contain polar groups are present to give hydrophilic properties to the globular protein, and it is anticipated that, when the details of the molecular structure are known, it will be found that amino acids such as serine are arranged along the chain so that, in the folded or globular form, they are able to present a maximum concentration of hydroxy groups to the surrounding medium.

As a natural continuation of this argument, it must be presumed that amino acid residues such as those of tryptophane, leucine, phenylalanine, and histidine are present in the molecule in order to play some definite part in the behavior of the molecule as a whole. This argument is further complicated by the recent findings of Smith and his colleagues at the Shirley Institute. These workers have found that the proportion of long side-chain amino acids to short side-chain amino acids differs considerably in the three main groups of silkworms, i.e., the tussah types of the *Antheraea* species, the silkworms of the *Bombyx* species, and those of the *Anaphe* species. The ratio is highest with the tussah fibroins and very low with the *Anaphe* fibroins, the *Bombyx* fibroins occupying an intermediate position. It is perhaps a confirmation of the hypothesis of the role of amino acid residues in the molecular behavior of fibroin that, with these different types of fibroins, the load-extension diagrams and other physical properties can be correlated with the distribution of amino acids.

Conclusion

Thus, despite our meager knowledge of the detailed chemical structure of the fibroin molecule, we can conclude that the molecule consists, in its extended form, of a polypeptide consisting of some 1000 or so amino acid residues. These long chains form antiparallel pleated sheets in accordance with the structural theories advanced by Pauling and Corey. Renaturation of the insoluble protein, i.e., to the form in which it occurs in the silk gland, is due to a macrofolding of the sheets of polypeptide chains so that the groups conferring hydrophilic properties on the molecule are mainly presented to the outside. Thus we have here a mechanism by which a globular protein can be unfolded and, by virtue of an extensive hydrogen bonding, can assume an insoluble fibrous form. This has obviously an important bearing on the production of regenerated protein fibers. It appears justifiable to conclude that, during the alkali maturation of proteins such as the peanut globulins, denaturation occurs not so much by a simple uncoiling process but more by a chemical hydrolysis resulting in a considerable rupture of the protein chains. This would mean that the product is not an intact protein but rather of the type of a primary or secondary proteose the viscosity of which is suitable for the spinning process. Brief reference can be made to two problems of interest concerning the denaturation of silk fibroin: first, that solutions of the water-soluble fibroin are not denatured when heated to 100°C for 10 min, as indicated by the constancy of the optical rotation. Second, the heat

changes during denaturation; Coleman and Howitt were unable to detect any evolution or absorption of heat during the spontaneous gelling of aqueous solutions of water-soluble fibroin, but this question merits reexamination owing to its important bearing on the extent and nature of hydrogen bonding during denaturation.

A final note must be made regarding the regeneration of fibroin fibers. Many workers have examined this possibility (see, for example, Wakeham et al. [9]), but so far the results have been disappointing. There are theoretical grounds for considering that silk fibroin could yield a regenerated fiber of tensile strength much greater than that achieved by the silkworm, which gently draws out through its spinnerets the fibroin present in the silk gland in the form of a gel of about 28% concentration [8]. Hori and coworkers in Japan have developed a method of spinning solutions of fibroin in caustic soda-ammonia-cupric hydroxide systems into acid baths, and this method has been explored commercially; a small sample of fabric thus produced was kindly sent to the author by Dr. Y. Suetsuga. Whether or not the regeneration of silk fibroin becomes a commercial possibility, there is little doubt that the mechanism of the formation of filaments from the water-soluble protein merits further study. Despite the fact that silk has been used by man for several thousands of years, there is much to be learned of its structure and behavior.

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The Preparation of Partially Cyanoethylated Cotton with Acrylonitrile

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Abstract

The preparation of partially cyanoethylated cotton with acrylonitrile in the presence of sodium hydroxide is described, including effects of changes in time, temperature, and concentration of reagents. Products with retention of the fibrous form have been obtained with degrees of substitution up to 2.7 cyanoethyl groups per anhydroglucose unit.

Hydrolysis of the cyanoethyl group occurs readily under alkaline conditions and results in both cleavage and conversion to the carboxyethyl group. Maximum conversion in the latter case was 29%.

THE cyanoethylation of cellulose with acrylonitrile was patented in 1938 [16], and several subsequent patents have covered various phases of the reaction. Somers [21] has reviewed work on cyanoethylation of cellulose with particular reference to attempts to use cyanoethyl cellulose which is soluble in organic liquids in the preparation of synthetic filaments.

Progress in the utilization of acrylonitrile has been deterred heretofore, because of the high cost of the reagent. However, recent production of acrylonitrile has now increased to the point where the cost has dropped markedly; the present relatively low cost

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of 31 cents per pound makes its use for the cyanoethylation of cellulose appear more attractive [24]. Interest in the subject has been renewed by recent publications of Compton and his coworkers [7, 8] at the Institute of Textile Technology, which cite improved textile properties, greatly enhanced heat and rot resistance, changed receptivity to dyes, and increased resistance to abrasion. The Southern Regional Research Laboratory is actively engaged in work on the chemical modification of cotton, and particularly in the production of partially acetylated cotton fiber [5, 9], which is already well known for its resistance to heat and to microorganisms. The comparative merits of these two products are not fully known at present. This laboratory is also interested in further modifications of partially cyanoethylated cotton. In these various modifications of cotton, its useful properties may be modified, however, with retention of its fibrous character.

The reaction of acrylonitrile with cellulose is unusual in that it is one of the few cases in which an unsaturated compound reacts with cellulose by vinyl addition. The addition takes place in the presence of strong alkalies, over a wide range of conditions. The reaction is as follows:

$$CH_2{=}CH{-}CN + Cell{-}OH \xrightarrow{NaOH} Cell{-}OCH_2{-}CH_2{-}CN$$

The principal purpose of the present paper is to describe the partial cyanoethylation of cotton cellulose with acrylonitrile under various conditions of time, temperature, and concentration. Such conditions have not been described previously in detail. Temperatures were varied from room temperature to the boiling point of the reagent mixture, and both pure acrylonitrile and the water-saturated mixture (about 3% water content) were used. For the purposes of study the concentrations of sodium hydroxide were varied over a wide range, although the high concentrations of alkali are probably impractical for commercial use. This is because of the increased wet pickup with consequent high formation of by-product β,β'-oxydipropionitrile (with poor recovery of acrylonitrile) and also because of the possibility of violent polymerization of the nitrile. Change in conditions yielded products with nitrogen contents of up to 12.3%, which corresponds to a degree of substitution (D.S.) of 2.7 cyanoethyl groups per anhydroglucose unit. Most of these products still retained the fibrous character of the original cotton.

Conditions under which cyanoethylated cotton may be hydrolyzed are also described, and an attempt was made to convert the cyanoethyl group quantitatively to the carboxyethyl group by hydrolysis, but with only partial success. The major reaction was complete removal of the cyanoethyl group; but some carboxyl groups were formed. This type of cleavage has also been noted by McGregor and Pugh [19], Hollihan and Moss [13], and Wright and Minsk [25]. However, contrary to McGregor [18, 20], except when a large conversion of the cyanoethyl groups to carboxyethyl groups had taken place, the authors did not in any case observe alkaline solubility of the cyanoethylated cellulose. McGregor's cyanoethyl cellulose was prepared from viscose with excess acrylonitrile and sodium hydroxide present. Probably both hydrolysis of the cyano group to carboxyl, and complete cleavage, occurred simultaneously, and the reaction continued with the excess acrylonitrile until a sufficient number of carboxyethyl groups had formed to cause solubility. Probably the relatively low degree of polymerization of the viscose used favored solubility, while the greater chain length of cotton makes products difficultly soluble.

It has been reported [14] that cyanoethyl ethers of cellulose with a D.S. of 2 to 3 will soften or dissolve in organic solvents such as acetone, pyridine, aniline, dimethyl formamide, methyl formate, and acrylonitrile. A piece of cloth, reacted to a D.S. of 2.7, was found to swell and become translucent in acetone but not to dissolve. Once again, the degree of polymerization is probably a deciding factor in determining the solubility.

Although acrylonitrile is both flammable and toxic, no difficulties were encountered when the usual laboratory precautions for handling such materials were observed. The flammable limits of the nitrile (3–17% by volume with air) approximate those of ethyl alcohol (4–19%) [10]. Good ventilation must be provided because acrylonitrile is approximately as toxic as hydrogen cyanide, the maximum allowable concentration being approximately 20 ppm in air [1]. If the nitrile comes into contact with the body, it should be washed off immediately, as it is absorbed through the skin [2].

Materials and Methods

A technical grade of acrylonitrile was used as received. Because of the toxicity and flammability of the nitrile [2], reactions were carried out in a fume hood. Cotton in the form of 12/5 sewing thread was used in most experiments. To assure that there

TABLE I. Effect of Change in the Concentration of Sodium Hydroxide on the Reaction of Cotton Cellulose with Acrylonitrile *

NaOH (%)	Pickup of NaOH Solution (%)	Weight Gain (%)	N† (calculated) (%)	N (found) (%)	D.S.‡	Breaking§ Strength (lb)	Breaking Strength (% of blank)
Blank	—	—	—	—	—	9.4	100
2	93	5.1	1.29	1.2	0.15	9.5	101
4	83	7.9	1.93	1.8	0.22	8.1	86
6	96	12.2	2.85	2.8	0.36	8.2	87
8	120	18.4	4.09	4.1	0.56	7.6	81
10	130	31.7	6.42	6.1	0.92	7.5	80
15	156	34.4	6.76	6.1	0.92	8.2	87
20	162	27.2	5.65	5.1	0.73	8.0	85
30	186	9.4	2.27	2.0	0.25	8.5	90

* Cotton impregnated with NaOH solution, centrifuged to wet pickup shown, then immersed in pure acrylonitrile for 30 min at room temperature (25–26°C).

† Calculated from weight gains.

‡ Calculated from nitrogen determination. D.S. (degree of substitution) is the average number of cyanoethyl groups per anhydroglucose unit.

§ Single-strand method A.S.T.M. D-180–52T.

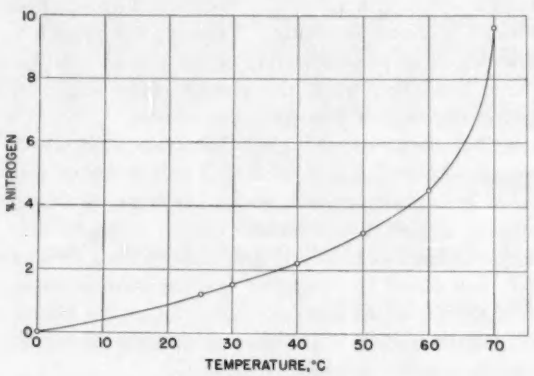

Fig. 1. Effect of variation in reaction temperature on the reaction of cotton cellulose with acrylonitrile. Cotton pretreated with 2% sodium hydroxide solution; then treated with acrylonitrile for 0.5 hr.

would be no complications due to impurities in the cotton, the thread was specially purified by extraction with ethanolamine [17].

The general procedure consisted of impregnating 20-yd skeins of thread, weighing about 4 g each, with a sodium hydroxide solution as specified, and centrifuging to about 85–90% wet pickup. A skein was then immersed in a 100 ml portion of acrylonitrile at the desired temperature and was maintained at this temperature for the specified time. The reaction was halted by plunging the sample into about 400 ml of 5% acetic acid solution. It was then washed with water and dried at 105°C.

TABLE II. Effect of Time on the Reaction of Cotton Cellulose with Acrylonitrile *

Time (min)	Weight Gain (%)	N (%)	D.S.†	Breaking Strength (lb)	Elongation (%)	Thickness (in.)
0‡	—	—	—	9.4	11.1	0.0274
0§	—	—	—	8.9	12.3	0.0289
10	8.2	2.2	0.28	8.8	12.5	0.0324
20	11.8	2.9	0.38	8.8	12.2	0.0307
30	15.6	3.6	0.48	7.9	13.7	0.0335
60	26.3	5.6	0.82	6.4	17.9	0.0371
180	45.6	8.1	1.35	5.8	21.2	0.0431

* Cotton thread impregnated with 2% NaOH solution, centrifuged to about 75% wet pickup, and treated with pure acrylonitrile at 55–60°C for the period of time shown.

† Calculated from nitrogen determination.

‡ Untreated thread.

§ Control thread, treated with 2% NaOH solution.

Carboxyethyl groups were determined by a titration method similar to that used for the determination of carboxymethyl groups in carboxymethyl cellulose [11]. Nitrogen determinations quoted in the paper are the average of two determinations of samples chosen at different points of the product. Agreement was good in most cases, generally within ±0.1% nitrogen content, showing good uniformity of treatment. At first, samples were analyzed for nitrogen by the usual Kjeldahl method. However, it was found that closely comparable results could be obtained if the sulfuric acid digestion step were eliminated and the samples simply distilled in the usual manner with the sodium hydroxide solution.

The degree of substitution (D.S.) shown in the tables was calculated from the nitrogen content using

the following formula:

$$\text{D.S.} = \frac{(162)(\%\text{N})}{1400 - [(53)(\%\text{N})]}$$

Effect of Variables upon the Reaction

Effect of Concentration of Sodium Hydroxide

Skeins, pretreated with sodium hydroxide of various concentrations, from 2 to 30%, were soaked in acrylonitrile at room temperature for 30 min. Results are shown in Table I.

It will be observed that analytical values of nitrogen content correspond fairly well with the values calculated from weight gain so the latter generally may be used as a guide to the amount of reaction.

As will be shown later, hydrolysis increases with increasing alkali concentration. Also, the reactions are competitive, so that at room temperature, as shown, maximum substitution is obtained at from 10–15% sodium hydroxide concentration.

Strength data were obtained on skeins which were free to shrink so it is probable that breaking strength results will differ according to the method of treatment. Strength has been compared with the untreated blank rather than to controls treated with sodium hydroxide since the alkaline treatment is part of the process. However, yarns treated with 2, 4, 10, and 20% sodium hydroxide at room temperature varied in breaking strength from 9.5 to 11.0 lb.

Effect of Temperature

With concentration of sodium hydroxide held constant at 2% and the time of reaction at ½ hr, the temperature was varied from 0 to 70°C. The latter is approximately the boiling point of the acrylonitrile-water azeotrope, which has been reported to be 70.7°C [12]. Results are shown in Figure 1.

At the highest temperature, substitution was almost two cyanoethyl groups per anhydroglucose unit.

Effect of Time

As shown in Figure 1, there is a large increase in the rate of reaction above 60°C. In order to minimize variations in reaction behavior caused by small differences of temperature in that range, the temperature of the reaction was kept between 55 and 60°C. Time was varied from 10 to 180 min. The results are shown in Table II. The reaction proceeded very rapidly at first, a D.S. of 0.28 being attained in the first 10 min. The succeeding degrees of substitution for 20, 30, 60, and 180 min are 0.38, 0.48, 0.82, and 1.35, respectively, showing a fairly regular reaction rate up to 0.82 with subsequent slowing of the reaction rate.

Effect of Concentration of Acrylonitrile

Since acrylonitrile is miscible in all proportions with benzene, this solvent was chosen as a diluent for a series of experiments in which the concentration of the nitrile was varied from 25 to 100%. Reaction times of 10, 20, 30, and 60 min were used, and the temperature was maintained at 55 to 60°C. Results are shown in Table III. It may be seen from the data that dilution of the nitrile with an inert solvent may be used to moderate the reaction so that a desired substitution may be obtained with less strict control of conditions.

Effect of Diluent

The effect of two other diluents besides benzene was investigated. Water, which is present in the sodium hydroxide solutions used, and tertiary butyl alcohol, which is often used as solvent in reactions involving acrylonitrile, were compared with acrylonitrile. In each case, 25 ml of the nitrile was used with 75 ml of diluent. The temperature was held at 55–60°C, and the mixtures were heated with samples for 10, 20, 30, and 60 min, respectively. The water-nitrile mixture was heterogeneous because the solu-

TABLE III. Effect of Dilution with Benzene on the Reaction of Cotton Cellulose with Acrylonitrile *

Reaction Time (min)	% Weight Gain with Acrylonitrile Percentages of				% Nitrogen Content with Acrylonitrile Percentages of				D.S. with Acrylonitrile Percentages of			
	25	50	75	100	25	50	75	100	25	50	75	100
10	4.4	6.3	7.9	8.2	1.3	1.6	1.8	2.2	0.16	0.20	0.22	0.28
20	5.9	8.6	10.3	11.8	1.5	2.1	2.3	2.9	0.18	0.26	0.29	0.38
30	7.2	10.2	11.5	15.6	1.7	2.5	2.6	3.6	0.21	0.32	0.33	0.48
60	9.7	11.7	14.1	26.3	2.3	2.8	3.1	5.6	0.29	0.36	0.41	0.82

* Pretreated with 2% NaOH.

TABLE IV. Effect of Different Diluents on the Reaction of Cotton Cellulose with Acrylonitrile

Reaction Time (min)	Diluent: Water* Weight Gain (%)	N (%)	D.S.	*tert*-Butyl Alcohol* Weight Gain (%)	N (%)	D.S.	Benzene* Weight Gain (%)	N (%)	D.S.	None (Pure Acrylonitrile) Weight Gain (%)	N (%)	D.S.
10	1.5	0.5	0.06	3.6	1.3	0.16	4.4	1.3	0.16	8.2	2.2	0.28
20	2.3	0.8	0.10	5.0	1.8	0.22	5.9	1.5	0.18	11.8	2.9	0.38
30	2.9	0.9	0.11	5.8	1.9	0.24	7.2	1.7	0.21	15.6	3.6	0.48
60	3.8	1.1	0.13	7.0	2.2	0.28	9.7	2.3	0.29	26.3	5.6	0.82

* 25 ml of acrylonitrile was diluted with 75 ml of solvent.

bility of acrylonitrile in water at this temperature is only about 9%. Nevertheless, results were reasonably uniform and it may be seen, in Table IV, that as might be expected the various diluents greatly decreased the amount of reaction.

In another set of experiments, acrylonitrile saturated with water at room temperature was used. Such a solution contains about 3% water, and its use is of considerable practical interest because the acryonitrile recovered by distillation from the cyanoethylation process would have this approximate composition. Skeins of purified 12/5 thread were treated with water-saturated acrylonitrile (recovered by distillation of used acrylonitrile, as detailed below). The skeins were impregnated as before with 2% sodium hydroxide solution, centrifuged, and treated for 10, 20, 30, and 60 min, respectively at two temperatures, 55 and 65°C. The skeins treated at the lower temperature contained 1.3, 2.3, 2.3, and 2.9% nitrogen, respectively. Cotton treated at the higher temperature had nitrogen contents of 1.6, 2.2, 2.7, and 3.7%, respectively. Comparison of these results with the figures given for pure acrylonitrile in Table IV shows that the pure nitrile is more reactive. However, water-saturated acrylonitrile may be used for treatment with slightly decreased effectiveness. For commercial applications, the use of the recovered acrylonitrile containing water would be much more economical than to attempt to obtain anhydrous acrylonitrile. Raising the temperature should help to increase the degree of substitution.

General Preparation of Partially Cyanoethylated Cotton

From the data given above it is evident that various combinations of conditions may be selected in order to partially cyanoethylate cotton cellulose according to the percentage pickup required.

Cloth Containing 4 to 5% Nitrogen

The work of Compton et al. [7, 8] indicates that nitrogen contents of 2 to 6% (weight pickups of 8 to 30%) cover the more practical range. Following are given the details of a typical preparation as performed at the Southern Regional Laboratory. To obtain a fabric in the 4 to 5% nitrogen range, open-boiled 48 × 48 sheeting (2.85 sq yd per lb) was soaked in 2% sodium hydroxide solution containing a wetting agent, and padded with two dips and two nips to 51% wet pickup. To aid in obtaining even penetration of the acrylonitrile, the cloth was then placed on glass cloth of equal size and the two were rolled together. The roll was placed in a reaction tube, and acrylonitrile was circulated through the tube at 55° ± 1°C for 90 min. An exothermic reaction was noted at the beginning of the reaction, and care was taken to prevent localized overheating by pumping the acrylonitrile at a rapid rate from the reaction tube, through a heat exchanger, and back to the tube. After completion of the treatment, the cloth was drained, the residual alkali neutralized with dilute acetic acid, and the neutralized cloth thoroughly washed with running tap water. The air-dry weight gain was 16%. Nitrogen determinations, made at two different points along the cloth, showed 4.28% and 4.34%, respectively. This corresponds to an average D.S. of 0.60 cyanoethyl groups per anhydroglucose unit.

Cloth Containing 9 to 12% Nitrogen

A typical preparation of cloth containing larger amounts of cyanoethyl groups is as follows: Samples

of 80 × 80 cotton print cloth (4.0 oz/sq yd) were padded to about 85% wet pickup of 10% sodium hydroxide solution and treated with acrylonitrile as before at 55°C. By treating for 2½ to 3½ hr, substitutions in the range of 1.7 to 2.7 cyanoethyl groups per anhydroglucose unit were effected. The samples on removal from the reaction tube were translucent and extremely swollen. However, after neutralization of the alkali and washing they still retained their fibrous form. The products with less than two substituents per anhydroglucose unit felt as though they had been lightly starched. The products with higher substituents, however, presented a parchmentlike appearance and were rather stiff.

Recovery of Acrylonitrile

Impure aqueous acrylonitrile may be purified by distillation yielding the azeotrope containing approximately 12% water. Part of this water separates on standing, leaving acrylonitrile containing about 3% water. A method of purification has been patented by Carpenter et al. [6].

The used acrylonitrile contains as impurities water, sodium hydroxide, reaction byproducts such as β,β′-oxydipropionitrile, and extractables such as wax, from the cotton.

The impure acrylonitrile was drawn off from a typical run, using 2% sodium hydroxide. It was immediately acidified with phosphoric acid to prevent further formation of β,β′-oxydipropionitrile. Distillation was carried out in the usual manner in a hot-water bath, the fraction distilling at 71–76°C being recovered. Calculated on the portion of liquid recovered, the yield of acrylonitrile was approximately 95%. A reddish-brown residue remained in the still pot. Care must be taken not to let this residue accumulate in the still pot, particularly if acetic acid has been used instead of phosphoric acid, because spontaneous polymerization may occur with evolution of heat and production of a voluminous sticky polymer which is extremely difficult to remove from the apparatus.

Acrylonitrile may be stabilized for storage by addition of a small amount of ammonia (0.01%), ammonium carbonate, hydroquinone, and other materials [1].

Hydrolysis of Partially Cyanoethylated Cotton

As stated above, hydrolysis of the cyanoethyl group either produces a carboxyethyl group or cleaves the cyanoethyl group from the cellulose residue. Various conditions of hydrolysis with alkali or acid as the hydrolyzing agent have been reported [3, 4, 13, 15, 19, 22, 23].

A cyanoethylated cotton with 6.2% nitrogen (D.S. 0.94) was selected and treated with different concentrations of alkali or with 50% formic acid under different conditions of time and temperature. Carboxyethyl and nitrogen determinations were made on the samples after the treatments. Results, as shown in Table V, indicate that some conversion of the cyano group to the carboxyl group takes place at room temperature with strong alkali and at elevated temperatures with formic acid. Heating of cyanoethylated cotton with dilute alcoholic potassium hydroxide, however, results in almost complete cleavage of the cyanoethyl group. Apparently, the cyano group sufficiently activates the ether linkage to cause cleavage to occur. When the cyano group is converted to carboxyl, the latter group has good stability toward hydrolysis.

Table VI shows the results obtained when a sample of cyanoethyl cellulose containing 2.3% nitrogen

TABLE V. Effect of Alkali under Different Conditions and of 50% Formic Acid on Hydrolysis of Partially Cyanoethylated Cotton and Cleavage of Cyanoethyl Groups

Treating Solution	Temp. (°C)	Time (hr)	N (%)	Carboxyethyl* (%)	Cyanoethyl Groups per Glucose	Carboxyethyl Groups per Glucose	Cyanoethyl Groups per Glucose Cleaved
None (control)	—	—	6.2	0.04	0.94	0.00	—
3% NaOH	25	72	0.8	3.97	0.10	0.09	0.75
5% NaOH	25	72	0.1	5.85	0.01	0.14	0.79
10% NaOH	30	1	5.8	0.25	0.86	0.01	0.07
0.05 *N* alc. KOH	75–80	1	0.1	0.34	0.01	0.01	0.92
50% Formic acid	90–95	1	5.8	1.48	0.86	0.03	0.06

* Determined by titration.

TABLE VI. Effect of Dilute Alkali at Different Temperatures on Hydrolysis of Partially Cyanoethylated Cotton and Cleavage of Cyanoethyl Groups

Treating Solution	Temperature (°C)	Time (hr)	N (%)	Carboxyethyl* (%)	Cyanoethyl Groups per Glucose	Carboxyethyl Groups per Glucose	Cyanoethyl Groups per Glucose Cleaved
None (control)	—	—	2.3	0.12	0.30	0.00	—
0.2% Soap							
0.2% Soda ash	ca. 100†	1	2.2	0.16	0.28	0.00	0.02
1% NaOH	ca. 25‡	1	2.2	0.12	0.28	0.00	0.02
1% NaOH	ca. 90–95§	1	0.3	0.53	0.04	0.01	0.25
1% NaOH	ca. 100†	1	0.1	0.58	0.01	0.01	0.28
2% NaOH	ca. 100†	1	0.0	0.79	0.00	0.02	0.28
3% NaOH	ca. 25‡	24	1.4	0.43	0.17	0.01	0.12
3% NaOH	ca. 25‡	72	0.8	1.07	0.10	0.02	0.18

* Determined by titration. ‡ Room temperature.
† Boiling temperature. § Steam bath temperature.

TABLE VII. Effect of Concentration of Sodium Hydroxide for 72 Hr at 5 and 25°C on the Hydrolysis of Cyanoethyl Cellulose and Cleavage of Cyanoethyl Groups

NaOH Conc. (%)	N (%)	Carboxyethyl* (%)	Cyanoethyl Groups per Glucose	Carboxyethyl Groups per Glucose	Cyanoethyl Groups per Glucose Cleaved
		At 5°C			
0	5.0	0.04	0.71	0.00	—
5	4.8	0.18	0.68	0.00	0.03
10	4.3	0.18	0.59	0.00	0.12
15	3.3	1.10	0.44	0.02	0.25
20	3.1	1.88	0.41	0.04	0.26
25	2.9	2.07	0.38	0.05	0.28
30	2.7	2.21	0.35	0.05	0.31
35	2.5	2.15	0.32	0.05	0.34
40	1.8	1.50	0.22	0.03	0.46
45	1.3	1.11	0.16	0.02	0.53
50	1.8	0.50	0.22	0.01	0.48
		At 25°C (Room Temperature)			
0	5.0	0.04	0.71	0.00	—
5	0.5	2.90	0.06	0.07	0.58
10	0.1	4.22	0.01	0.10	0.60
15	0.0	3.90	0.00	0.09	0.62
20	0.0	4.16	0.00	0.10	0.61
25	0.1	4.84	0.01	0.11	0.59
30	0.0	4.23	0.00	0.10	0.61
35	0.0	3.49	0.00	0.08	0.63
40	0.1	2.36	0.01	0.05	0.65
45	0.1	1.07	0.01	0.02	0.68
50	0.1	0.61	0.01	0.01	0.69

* Determined by titration.

was subjected to dilute alkaline hydrolysis at different temperatures and reaction periods. Hot dilute alkaline solutions remove practically all the cyanoethyl groups with little formation of carboxyethyl groups. On the other hand, removal of the cyanoethyl group is much less complete at room temperature, although after 72 hr 66% of the groups have been hydrolyzed. The cloth exposed to soap and soda ash at 100°C for 1 hr lost little nitrogen.

TABLE VIII. Effect of Reaction Time on the Hydrolysis of Cyanoethyl Cellulose and Cleavage of Cyanoethyl Groups by 25% Sodium Hydroxide at Room Temperature

Time (hr)	N (%)	Carboxyethyl* (%)	Cyanoethyl Groups per Glucose	Carboxyethyl Groups per Glucose	Cyanoethyl Groups per Glucose Cleaved	Moisture† Regain (%)
0	3.4	0.15	0.45	0.00	—	3.9
½	3.4	0.30	0.45	0.00	0.00	8.5
1	2.9	0.51	0.38	0.01	0.06	9.2
2	2.5	1.17	0.32	0.03	0.10	9.9
4	1.9	2.63	0.24	0.06	0.15	10.6
16	0.1	5.51	0.01	0.13	0.31	11.0
24	0.1	5.56	0.01	0.13	0.31	10.8
48	0.0	5.67	0.00	0.13	0.32	10.6
72	0.0	5.00	0.00	0.12	0.33	10.6

* Determined by titration.
† Conditioned at 70°F and 65% R.H.

To determine optimum conditions for conversion of the cyano group to carboxyl, a sample of cyanoethylated cotton containing 5.0% nitrogen was divided into 20 equal portions each weighing about 2 g. Ten of the portions were placed in sodium hydroxide solutions of 5 to 50% concentration, respectively, and allowed to stand at room temperature (ca. 25°C) for 72 hr. A duplicate set was held at 5°C for the same period of time. Results are shown in Table VII. At either 5 or 25°C, maximum conversion of the cyano group to carboxyl occurred at about 25% sodium hydroxide; this represents a conversion of 15.5%. Next, the effect of time was investigated under these optimum conditions. In Table VIII are shown the results obtained on hydrolysis of a sample

containing 3.4% nitrogen with 25% sodium hydroxide at room temperature. The extent of hydrolysis increases up to 16 hr, when it is essentially complete with about a 29% conversion of cyanoethyl group to carboxyethyl group. Moisture regain of the hydrolyzed product is greatly increased over that of the untreated cellulose and of the cyanoethyl cellulose. The latter has been observed to have low moisture regain [8]. The high moisture regain observed in this case is probably due both to mercerizing action by the strong alkali and to formation of sodium carboxyethyl groups. Sodium carboxymethyl cellulose is known to have a high regain [11].

Summary and Conclusions

Conditions necessary for the partial cyanoethylation of cotton have been studied and reported. The effects of changing time of reaction, temperature, diluents, and concentration of reagents have indicated that the reaction may be controlled to give almost any degree of substitution desired without destroying the fibrous form of the cotton. Although for most textile uses products with less than one cyanoethyl group per anhydroglucose unit are desirable, substitutions up to 2.7 groups per glucose unit have been obtained. Typical laboratory-scale preparations of partially cyanoethylated cotton cloth are given.

Cleavage of the entire cyanoethyl group is easily accomplished, but its conversion to the carboxyethyl group is attained with poor efficiency. Alkaline hydrolysis results largely in cleavage of the cyanoethyl group at the ether linkage. With 25% sodium hydroxide solution, reacting for 16 hr, a maximum conversion of 29% of the cyanoethyl groups to carboxyethyl groups was obtained.

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Distribution of the Substituents in Heterogeneously Methylated Celluloses

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Abstract

Four methyl celluloses made from cotton linters with dimethyl sulfate and alkali in toluene and one commercial product were hydrolyzed. Unsubstituted, monomethyl, dimethyl, and trimethyl glucose in the hydrolyzates were separated by filter paper chromatopile, and the results were compared with the calculated values of Spurlin and the experimental values of other investigators.

Introduction

So far, many investigations [2, 6] have been made on the methylation of cellulose, but most of them merely discussed the effect of conditions of methylation on the degree of substitution. Distribution of the methoxyl groups of methyl celluloses was discussed in 1936 by Traube, Piwonka, and Funk [8], and in 1948 by Timell [7] in detail. They fractionally distilled the mixture of methyl glucosides obtained by methanolysis of methyl celluloses. That complete separation of the methyl glucosides by the distillation method would be difficult was foreseen by Spurlin [5].

In previous experiments [4], the authors succeeded in complete quantitative separation of methyl glucoses by filter paper chromatopile. Then the chromatographic method was applied to heterogeneously methylated celluloses, and distribution of the substituents was discussed.

Experimental Procedures and Results

Cotton linters were methylated with dimethyl sulfate and 35% sodium hydroxide in toluene, and 5 samples were obtained (Table I).

TABLE I. Methoxyl Content of Methyl Celluloses

Sample No.	OCH_3 (%)	D.S.
1	8.15	0.44
2	17.4	0.99
3	27.5	1.64
4	31.0	1.88
5	32.6	2.00

Sample 1. Ten grams of air-dried cotton linters were suspended in 380 cc of toluene, 40 cc of 35% sodium hydroxide were added, and the mixture was kept standing for 2 hr in an atmosphere of nitrogen. Then 35 g of dimethyl sulfate were added, and the methylation was continued for 2 hr at 30°C.

Sample 2. Ten grams of air-dried cotton linters were immersed in 35% sodium hydroxide for 1 hr at 30°C. The alkali cellulose, compressed to five times the original weight, was suspended in 380 cc of toluene, 50 cc of dimethyl sulfate were added, and the mixture was methylated for 6 hr at 30°C.

Sample 3. Sample 2 was remethylated under the same conditions.

Sample 4. Sample 3 was remethylated under the same conditions.

Sample 5. Sample 4 was remethylated under the same conditions.

Four of these five samples and a commercial product (Dow Chemical Corp.) were used. Each of these samples was hydrolyzed with 70% sulfuric acid for 3 days at room temperature and diluted to about 1% acid and refluxed for 24 hr. The solution was neutralized with barium carbonate and concentrated under vacuum, and the methanol extract of the syrup was dried on phosphorus pentoxide.

Any hydrolyzate processed as above produced four spots by linear paper chromatography. The solvent was a mixture of butanol and methanol (4:1). The rate of flow values of unsubstituted, monomethyl, dimethyl, and trimethyl glucose were 0.28, 0.53, 0.77, and 0.91, respectively. The most highly methylated cellulose (D.S. 2.0) also included a considerable quantity of unsubstituted glucose.

The quantitative separation was attained by chromatopile [4]. The apparatus used is shown in Figure 1. One thousand sheets of filter paper previously extracted with methanol to remove resins were used. The solvent was the same as that for paper strips, and time for development was 48 hr at 20°C. After the development, every tenth filter paper was taken out and a fragment of it colored with aniline phthalate. The zones where sugars were present were separated and extracted with methanol in the apparatus used for the development. The methanol solutions were evaporated to dryness and weighed. The mole percentages of glucose and its derivatives from 5 methyl celluloses are shown in Table II.

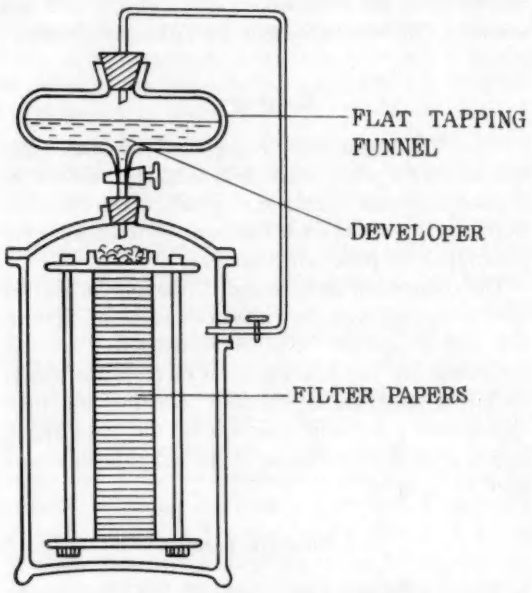

Fig. 1. Apparatus for chromatopile.

Discussion

The low-methylated cellulose (D.S. 0.44) was composed of unsubstituted (72.4%), monomethyl (15.6%), dimethyl (5.2%), and trimethyl (6.8%) glucose. The content of unsubstituted glucose decreases, and those of dimethyl and trimethyl glucose increase, as the degree of substitution increases. Even the most highly methylated cellulose (D.S. 2.0), however, includes 4.5% unsubstituted glucose. These results are compared with the values calculated by Spurlin [5] on the assumption that the substituents are distributed according to the law of chance, and with the results by Traube et al. [8], and those by Timell [7], in Figure 2.

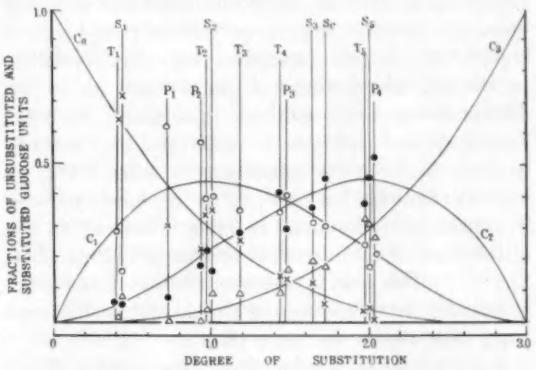

Fig. 2. Fractions of unsubstituted and substituted glucose units in methyl celluloses. The symbols *S*, *T*, and *P* represent methyl celluloses obtained by the authors, Timell, and Traube, respectively. Mole fractions in the hydrolyzate are represented by × = glucose; ○ = monomethyl glucose; ● = dimethyl glucose; △ = trimethyl glucose. C_0, C_1, C_2, and C_3 are curves calculated by Spurlin for random distribution of glucose, monomethyl, dimethyl, and trimethyl glucose, respectively, assuming the ratio of reactivities of the three hydroxyl groups to be 1:1:1.

TABLE II. Glucose and Its Methyl Derivatives Contained in the Hydrolyzates of Methyl Celluloses

Sample No.	D.S.	Theoretical Yield of Hydrolysis (%)	Composition of Hydrolyzate (mole %)			
			Unsubstituted Glucose	Monomethyl Glucose	Dimethyl Glucose	Trimethyl Glucose
1	0.44	96.5	72.4	15.6	5.2	6.8
2	0.99	95.0	35.6	39.8	16.0	8.6
3	1.64	94.9	12.8	31.1	36.5	19.6
C	1.72	95.6	5.9	30.1	46.4	17.6
5	2.00	96.5	4.5	18.1	46.3	31.1

Sample *C* was a commercial product; the weight of sample for hydrolysis was about 1 g.

The figure shows that the content of monomethyl glucose in the two methyl celluloses of low extent of reaction (P_1 and P_2) investigated by Traube et al. is considerably higher than that calculated. This may be due to the methylating condition (methylation of sodium cupricellulose), as pointed out by Spurlin. The results by Timell are approximately the same as the theoretical, although some deviation can be observed.

The authors' investigation shows that, in the low extent of reaction (S_1 and S_2), the contents of unsubstituted glucose and trimethyl glucose are much higher than those calculated, which the observed values approach as the reaction proceeds. This indicates that, in the initial stage of methylation, only the accessible part of cellulose reacts with the reagent, giving higher contents of unsubstituted and trimethyl glucose. As the degree of substitution becomes higher, the reagent penetrates into the crystalline region and the contents of glucose and its methyl derivatives approach to those calculated. Then the heterogeneous methylation such as the author's worked on is in its initial stage rather being an intermicellar reaction; and, as the reaction proceeds, it approaches permutoid reaction, resulting in the distribution of the methoxyl groups as calculated by Spurlin. This means the methylation takes place also in the crystalline region, and all hydroxyl groups react with almost the same chance.

The commercial product has more uniform distribution, indicating that the methylating reagent used penetrates into the crystalline region even in the initial stage of the reaction.

The above-mentioned conclusion is confirmed when the solubilities of the methyl celluloses are compared (Table III). Whereas the commercial product shows complete solubility in water and glacial acetic acid, the product of D.S. 1.62 only swells and that of D.S. 2.00 dissolves, resulting in turbid solutions in these solvents. Thus the commercial product is believed to have a more uniform distribution of the substituents and good solubility, as expected from the observation by Bock [1] that in a quarternary ammonium hydroxide solution homogeneously methylated cellulose shows complete solubility in water in spite of its low degree of substitution (D.S. 0.7).

So far, the authors have not succeeded in separating the isomers of monomethyl and dimethyl glucose by chromatography, although some of them were separated by Hirst, Hough, and Jones [3]. They intend to continue and develop this investigation and to determine the reactivity of one primary and two secondary hydroxyl groups of each glucosidic residue.

TABLE III. Solubility of Methyl Celluloses

Sample No.	1	2	3	5	C
D.S.	0.44	0.99	1.64	2.00	1.72
Solubility					
Water	slight	medium	strong	turbid	clear
5% NaOH	slight	medium	strong	turbid	turbid
Ethanol	slight	medium	strong	strong	strong
Acetone	slight	slight	medium	medium	strong
Chloroform	none	none	none	slight	medium
Toluene	none	none	none	none	none
Glacial acetic acid	strong	strong	strong	strong	clear
Pyridine	slight	medium	strong	strong	strong

The terms none, slight, medium, and strong refer to the degrees of swelling, and the terms turbid and clear to the state of the solutions.

Summary

Four heterogeneously methylated celluloses from cotton linters with alkali and dimethyl sulfate in toluene and one commercial product were hydrolyzed, and the components of each hydrolyzate were determined by paper chromatopile.

The contents of glucose and its methyl derivatives were compared with the values calculated by Spurlin and with the results by other investigators. It was concluded that the heterogeneous methylation was in its initial stage an intermicellar reaction and then approached permutoid reaction in the later stage, resulting in the distribution of the substituents calculated by Spurlin.

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The Effect of the Distribution of Methoxyl Groups upon Some Textile Properties of Methylated Cotton Fiber[1]

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Contribution from the Southern Regional Research Laboratory, New Orleans, Louisiana[3]

AN EXAMINATION of the influence of the distribution of ether-linked substituents upon the textile properties of modified cotton fiber has been undertaken at the Southern Regional Research Laboratory. The purpose of this study is to assist in the selection of reaction conditions which will lead to the development of useful, partially etherified, modified cottons. For various reasons, some of which are mentioned below, it was decided to study first the influence of distribution of methoxyl groups upon textile properties. The investigation may later be extended to include such ether-linked substituents as cyanoethyl, hydroxyethyl, carboxymethyl, and others.

Although the very first methylation of cellulose by Suida [6] was undertaken for the purpose of modifying a textile property in cotton fiber, very little of the subsequent published work has had this expressed purpose. As a consequence there is in the literature no systematic evaluation of the changes in textile properties of cotton which accompany the introduction of increasing amounts of ether-linked methoxyl groups. There is, however, good evidence that the textile properties of methylated cotton will be strongly dependent upon the method employed for the introduction of the substituent. For example, Sitch [5] notes that methylation in the range of 19 to 26% methoxyl may produce water-soluble, or water-insoluble, methyl cellulose, depending upon the method of introduction of the methoxyl groups. Observations such as this point to the possible importance of the distribution of substituents in the methylated fiber.

Other practical considerations which influenced the selection of methylated cotton for this study were the following: Methyl groups can be readily introduced into cotton under relatively nondegrading conditions. The substituents are very stable against acid or alkaline cleavage. The analysis for methoxyl is relatively straightforward and simple in comparison with that of many of the other ether-linked substituents which might be considered. And finally, all the methyl glucoses resulting from the hydrolysis of the methylated cotton are known substances, whereas this is not so with most of the other substituents.

This report is divided into two sections. The first section is concerned with two widely different processes for the methylation of cotton and with some of the changes in textile properties which accompany the introduction of increasing amounts of methoxyl by the two processes. The second section is concerned with the distribution in the fiber of methoxyl groups introduced by the two different processes described in the first section.

The Preparation of Methylated Cotton Threads and Some of Their Textile Properties

Materials and methods. For convenience in carrying out tensile tests on relatively small amounts of treated materials this work was done with commercial sewing threads. The threads were selected for their uniformity and balanced twist. One thread contained 5-plied No. 12 yarns (12/5) of native cotton; the other was a mercerized 2-cord thread. The threads were subjected to treatments in the form of 25-, 50-, or 100-yd skeins.

Tensile tests were made on a Suter yarn tester, each recorded value representing the average of approximately ten breaks. The dry samples had been conditioned to the laboratory atmosphere, the

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wet samples had been thoroughly soaked in water and were tested immediately after removal from the water.

Methoxyl analyses were made on the air-dried materials by a standard Zeisel procedure [1] modified by the omission of phenol. Moisture was determined by oven drying at 105°C, and the methoxyl content of the dry material was calculated and employed to calculate the degree of substitution (D.S.), i.e., the average number of substituents per glucose anhydride unit.

Methylation with ethereal diazomethane was accomplished under a variety of conditions similar to those described by Reeves and Thompson [7], Head [4], and Sitch [5], and in addition in some instances the methylation was conducted at room temperature instead of under refrigeration. Increasing the moisture content of the cotton or of the reaction medium as recommended by Head and Sitch resulted in a more rapid rate of reaction. Increasing the temperature also increased the rate of reaction.

TABLE I. Breaking Loads of Diazomethane Methylated Cotton Thread

% Methoxyl (Air Dried)	D.S.	Breaking Load (lb) Dry	Wet
	Mercerized Thread		
3.95	0.22	9.6	9.1
4.72	0.25	9.2	9.2
5.63	0.32	9.3	8.6
6.15	—	10.1	9.4
6.45	—	8.6	8.5
6.57	—	9.7	9.2
6.72	0.38	9.1	8.6
7.64	0.44	9.0	8.6
8.20	0.46	9.3	8.7
9.72	0.56	8.4	8.0
11.07	—	9.0	8.4
11.43	—	9.2	8.5
11.97	0.70	9.0	9.0
12.85	0.75	9.0	8.1
14.46	0.85	8.8	7.6
15.98	0.95	7.9	7.6
Control (ether)		9.1	9.7
Blank (no treatment)		9.2	9.2
	12/5 *Thread*		
2.33	—	8.3	11.2
2.86	—	8.8	10.5
3.46	0.16	8.3	9.9
5.00	0.26	9.6	10.3
6.16	—	10.5	10.7
6.58	0.38	9.1	10.0
8.24	0.46	8.2	9.9
Control (ether)		10.2	11.4
Blank (no treatment)		9.6	11.5

However, since no property differences were observed which were attributable to the small differences in conditions of diazomethane methylation, the products are designated only by their methoxyl content. By varying the length of treatment, the number of successive treatments, and the concentration of reagent, samples of mercerized thread were prepared ranging from 3.95 to 15.98% methoxyl; and of 12/5 thread, from 2.33 to 8.24% methoxyl.

Methylation with dimethyl sulfate was accomplished by padding skeins of the 12/5 yarn in 45% sodium hydroxide, wringing to approximately 200% pickup, and then immersing in a bath of toluene containing 0.5 mole of dimethyl sulfate for each mole of sodium hydroxide in the thread. The bath had previously been brought to 84–87°C, and the heat of reaction or heat externally applied served to hold the bath at this temperature, which is roughly the boiling point of the toluene-water azeotrope. After reaction for various intervals from 5 to 30 min the skeins were removed from the bath, tested with phenolphthalein, and found to be strongly alkaline. They were then placed in a boiling solution of sodium carbonate. The skeins were next washed free of alkali with successive changes of boiling water, after which they were oven dried at approximately 100°C.

The wet and dry breaking loads of the methylated threads are given in Tables I and II. Table I lists these properties for the diazomethane methylated mercerized and native threads. This type of methylation produced no significant change in dry breaking load up to a methoxyl content of approximately 16%; in wet breaking loads there was at most a very slight decrease at the higher methoxyl contents. As previously noted [7], greater methoxyl contents were achieved with mercerized than with native cotton.

TABLE II. Breaking Loads of Cotton Thread Methylated with Sodium Hydroxide and Dimethyl Sulfate in Toluene at 84–87°C

% Methoxyl (Air Dried)	D.S.	Breaking Load (lb) Dry	Wet
1.24	0.05	9.32	9.86
3.61	0.19	9.41	8.70
6.60	0.32	9.08	8.96
7.77	0.44	8.35	8.56
9.80	0.55	8.37	4.39
12.06*	0.70	7.94	3.88
Alkali treated control		9.46	9.62

* In this experiment the molar ratio of dimethyl sulfate to sodium hydroxide was 1:1.

There is no indication that the tensile properties of native and mercerized threads were differently affected by diazomethane methylation.

Table II lists the dry and wet breaking loads for 12/5 threads methylated under mercerizing conditions with dimethyl sulfate and strong alkali. Although there was no great change in dry strength up to 12% methoxyl there was a very pronounced loss of wet strength beginning at about 10% methoxyl.

Stiffness in the methylated threads. It was noted that at the higher methoxyl contents the dimethyl sulfate methylated samples were very appreciably stiffened, whereas this effect in the case of the diazomethane methylated samples was barely perceptible.

Rot resistance of the methylated threads. This property was investigated in soil-burial experiments using diazomethane methylated and dimethyl sulfate methylated samples. All the latter, like the untreated threads, were completely decomposed within 1 wk in the soil-burial beds; however, the diazomethane methylated samples showed increased rot resistance with increasing methoxyl content. Some results of this work are shown in Table III.

This finding is in agreement with an earlier statement that diazomethane methylated cotton shows great resistance against the action of a cellulose-decomposing bacteria [7].

The Distribution of Methoxyl Groups in Methylated Cotton

The results described in the preceding section confirm the expectation that different textile properties may be produced in cotton by different types of methylation processes. At the level of 12 to 12.5% methoxyl (D.S. approximately 0.7) methylation with diazomethane yielded a product which retained its original dry and wet strength and had greatly increased rot resistance. Methylation to the same extent with dimethyl sulfate and strong alkali greatly reduced the wet strength and failed to confer appreciable rot resistance.

TABLE III. Soil-Burial Experiments with Diazomethane Methylated Mercerized Cotton Thread

Percent Methoxyl (Air Dried)	4.72	6.75	11.97	14.46
	Breaking Load (lb)			
Before burial	9.2	9.4	8.3	8.8
After 1 wk burial	8.2	8.5	8.5	—
After 2 wk burial	6.8	8.5	8.8	8.4
After 4 wk burial	Decomposed	7.1	8.7	8.9
After 6 wk burial	Decomposed	7.1	8.9	8.9

Since it appeared likely that the large differences in textile properties noted above might be the result of differences in the location of the substituents within the cotton fibers, the distribution of the methoxyl groups was investigated. Two different procedures were employed. In the first procedure the methylated product was drastically hydrolyzed to monosaccharide units, and the fermentable reducing sugar in the hydrolyzate was determined. This gives a measure of the relative proportion of substituted and unsubstituted glucose units in the methylated products. In addition to the two types of methylated cottons described in the preceding section, samples of commercial, alkali-soluble methyl cellulose were investigated by this method.

The second method of studying the distribution of methyl groups in methylated cottons involved partial hydrolysis experiments in which weight loss and methoxyl content of the residues were determined. The purpose of employing this method was to discover which of the two types of methylation described in the preceding section tended to concentrate substituents more extensively in the accessible regions of the fiber.

Total hydrolysis and fermentation. The following experimental conditions were adopted for this work: Approximately 200 mg of methylated cotton or methyl cellulose were dissolved in 1 ml of 73% sulfuric acid and allowed to stand in a tightly stoppered test tube at room temperature for 6 to 7 days. Five milliliters of water was then added and the resulting solution was heated in a boiling water bath for 75 min. This solution was rinsed into a small beaker, 1 ml of normal acetic acid was added, and the solution was brought to *p*H 4.0 to 4.5 with approximately 5 ml of 5 *N* potassium hydroxide. After neutralization the solution was made to exactly 50 ml, and 10 ml were withdrawn for reducing sugar determinations. The remainder of the solution was stirred with approximately 200 mg of yeast powder and allowed to ferment at room temperature for 3 days, after which it was centrifuged and the reducing sugar was again determined. It was important that the same size aliquot be employed both before and after fermentation, because the reduction of the methyl glucose components of the solution is not necessarily linear with concentration. It was con-

firmed, in separate experiments, that the yeast did not ferment the methylated glucoses.

The actual reducing sugar determinations were made on an aliquot amounting to 1% of the total hydrolyzate. The Hanes modification of the Hagedorn-Jensen method was employed [3]. The standard glucose solution was prepared by dissolving pure glucose in a salt solution having the same composition as the hydrolyzate and adjusting to the same *pH* range. The difference between reducing sugar values before and after fermentation is called "apparent fermentable glucose."

The values obtained for fermentable reducing sugar were recalculated to the basis of milligrams of "apparent fermentable glucose" per gram of anhydrous methyl cellulose. These values are plotted as ordinate in Figure 1 against the degree of substitution, which represents the average number of substituents per glucose unit in the original methyl cellulose.

It is evident that all the points in Figure 1 lie, within experimental error, on a single curve, irrespective of the method of preparation of the methyl cellulose. From these results it may be concluded that, within the range of methoxyl contents investigated, the method of methylation did not greatly influence the amount of unsubstituted glucose at any particular degree of substitution.

The partial hydrolysis of methylated cotton. Sitch [5] has recently reported data on the weight loss and methoxyl content after partial hydrolysis of a methylated cotton prepared by the action of diazomethane on mercerized cotton fiber. The conditions employed by Sitch were adopted for the present work, namely, hydrolysis by 0.5 *N* sulfuric acid at 90°C. Sitch's findings on diazomethane methylated mercerized cotton were confirmed, and extended to cover diazomethane methylated native cotton and dimethyl sulfate methylated cotton as well. These results are shown graphically in Figure 2. In this figure the methoxyl content of the hydrolyzed residue is plotted as ordinate against the weight loss as abscissa. Curve *A* represents data obtained with one of the dimethyl sulfate methylated threads described in a preceding section. Curve *B* represents Sitch's published data obtained with mercerized, diazomethane methylated cotton. Curve *C* represents diazomethane methylated native cotton.

Inspection of Figure 2 clearly indicates that in diazomethane methylated cotton the substituents are the more concentrated in those regions of the fiber

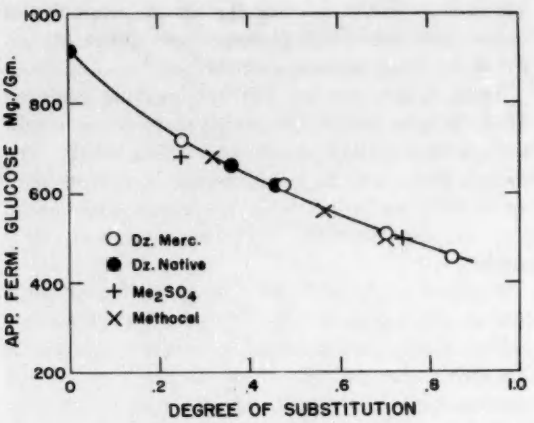

Fig. 1. The "apparent fermentable glucose" as a function of degree of substitution for cotton methylated by diazomethane and dimethyl sulfate, and for alkali-soluble commercial methyl cellulose.

which are accessible to acid hydrolysis. There was an immediate decrease in methoxyl content of the residue upon acid hydrolysis. The dimethyl sulfate methylated fibers, on the other hand, suffered a considerable weight loss before a significant reduction in methoxyl content became apparent. As Sitch has shown, this loss of methoxyl is not due to the cleavage of ether linkages, but is due to the dissolution of the methylated glucose units.

Discussion

This work has demonstrated the fact that different textile properties may be imparted to cotton by different types of methylation processes. In explanation of this fact the following possibilities must be considered: First, the different processes may degrade the cellulose to different extents. Second, the different properties may be the result of the different distributions of the substituents within the fibers. It is, of course, possible that the different properties might be due to a combination of the two possibilities.

With regard to the possibility of cellulose degradation, Sitch [5] has concluded that cellulose degradation does not occur upon diazomethane methylation. The possibility of cellulosic degradation in the dimethyl sulfate methylation processes cannot be entirely eliminated at the present time; however, conditions employed in this process were carefully chosen to minimize this possibility. The thread was never allowed to come in contact with acid conditions, and the vigorously boiling toluene-water azeo-

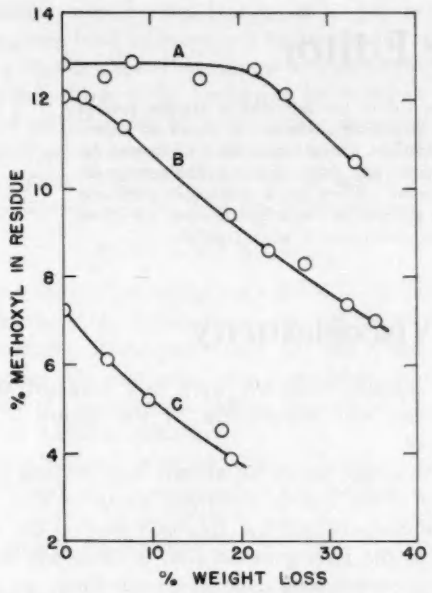

Fig. 2. The changes in methoxyl content upon partial hydrolysis of methylated cottons. Curve *A*, methylated with dimethyl sulfate and alkali. Curve *B*, mercerized cotton methylated with diazomethane (Sitch, [5]). Curve *C*, native cotton methylated with diazomethane.

trope was counted on to protect against atmospheric oxygen. That significant degradation did not occur during either methylation process is strongly indicated by the fact that the dry strengths of the products were not greatly lowered.

The possibility that the different distribution of methoxyl groups in the two types of methylated products affects their textile properties provides an attractive explanation for the greater rot resistance of the diazomethane methylated fibers inasmuch as methylation with this reagent produces a concentration of substituents in the accessible regions of the fiber where substituents are most effective in inhibiting the attack of the rotting microorganisms. Conversely, it may be argued that dimethyl sulfate methylation leaves many unmodified glucose units in the accessible regions and that these are susceptible to attack by the rotting organisms. A similar conception has been advanced by Goldthwait, Buras, and Cooper [2] to explain the rot resistance of partially acetylated cotton.

The stiffness and lower wet strength of the dimethyl sulfate methylated fibers probably result from a greater disorganization of the original crystallite structure resulting from the deeper penetration of substituents into the fiber. It has previously been shown, for mercerized cellulose, that the X-ray pattern is more extensively altered by dimethyl sulfate methylation than by diazomethane methylation [7].

Conclusion

It appears that the distribution of substituents may be of primary importance in determining the textile properties of modified cottons. For retention of desirable textile properties and improvement of rot-resistant qualities, substitution in the range of 0.25 to 1.0 per glucose unit should preferably be carried out under minimum swelling conditions. Swelling conditions, of course, increase the rate of substitution reactions, but they may produce undesirable properties in the methylated product and reduce the effectiveness of the rot resistance.

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

A Note on Nonlinear Viscoelasticity

TEXTILE CHEMISTRY LABORATORIES
The University, Leeds, England
November 10, 1954

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Since all solid materials exhibit viscoelastic behavior of some sort, it must be a fundamental property of the molecular structure of matter. Interpretations of viscoelasticity based on mechanical models of springs and dashpots often require many such elements to describe the observed behavior adequately and only transfer the problem to that of the elasticity of the springs and the viscosity of the liquids in the dashpots, without providing any real explanation. While the macroscopic structure may play an important part in determining the scale on which these effects manifest themselves, the chemical constitution of the substance must be the ultimate factor.

Molecular explanations of the elastic properties of crystals and the viscosity of perfect liquids are well known, but similar treatment of the rheology of amorphous or semiamorphous solids (rubber and textile fibers) is fairly recent [1, 3, 7, 8]. In the latter, the number of elements required to provide a fair quantitative agreement between experiment and theory has been successfully reduced to three: two springs and one dashpot. This was achieved by applying reaction-rate theory by treating flow as a bond-breaking/bond-formation reaction, from which it was shown that the rate of flow of the dashpot should be proportional to the hyperbolic sink of the stress (Eyring viscosity) instead of directly to the stress, as would occur with a Newtonian liquid. The springs, however, were still assumed to be Hookean and independent of the nature of the dashpot.

A two-state model has already been devised [2, 5] which exhibits both nonlinear elasticity and nonlinear viscosity, but the approach was on the same lines as the Eyring model and, to bring the theory into agreement with data on keratin fibers, an additional independent Hookean spring had to be introduced in series with the two-state model. Arbitrary non-Hookean springs have also been postulated to bring the theoretical predictions of the three-element model into better agreement with experimental data [3], but there is little to be said in favor of such approaches. The use of non-Hookean springs, however, should not be abandoned if a satisfactory molecular basis for them can be provided. One may thus regard the statistical-kinetic theory of rubber elasticity as providing a nonlinear spring, but it is based on an initially randomly kinked molecular chain where entropy changes determine the stress-strain behavior; the two-state model, however, presupposes a regularly folded molecular chain, and the major factor is the internal energy of the system as in most elastic bodies.

It is my aim here to show that it is possible to predict a quantitative relationship between elastic and viscous behavior from a general picture of solids as polymolecular networks of valence bonds. From this it then follows that rheological effects are a universal property of all condensed matter, and only because their time scales are so enormous do some substances appear to be purely elastic; liquids far from their boiling points are thus similar to solids but have extremely brief time scales. Before proceeding to the new approach, however, it will be useful to summarize the previous position.

Tobolsky, and Eyring, Halsey, et al. [3] regard each valence bond as equivalent to the bonded atoms being at the bottom of an energy well of depth F_0^*. The energy level of the atoms can be raised by the stress f until the rate of bond rupture is accelerated sufficiently for relaxation or flow to be apparent. By assuming that the stress reduces the activation energy barrier linearly, they reach the relation:

$$F^*/kT = F_0^*/kT - \alpha f \tag{1}$$

where $\alpha = v/kT$, v being the molecular volume of the flow unit, k, Boltzmann's constant, and T the temperature. Burte and Halsey [2] and Peters and Speakman [5] also make this assumption, whereas Prandtl [6] assumes the barrier to decrease linearly with the bond deformation.

Let us assume, however, that the bond activation energy barrier F^* varies when the bond length is stretched from its equilibrium value z_0 to a length z, according to the equation

$$F^* = F_0^*(2e^{-ar} - e^{-2ar}) \tag{2}$$

where $r = (z - z_0)/z_0$ and a is a molecular constant characteristic of the bond involved. The justification for using this equation is that it has the same form as the well-known Morse equation for changes in the *internal* energy of bonds, an equation which has proved valuable in inte preting spectroscopic data in terms of force constants and bond energies. The force, in dynes, acting on each bond to reduce the barrier is $-\partial F^*/\partial z$, when F^* is expressed in ergs per molecule and z in centimeters. This force is proportional to the total stress divided among the n bonds which are bearing the load in a given cross section. If each bond occurs in an area x_0y_0, the force per unit area of the specimen (f) is then given by:

$$f = \frac{2anF_0^*}{v}(e^{-ar} - e^{-2ar}) \tag{3}$$

where $v = x_0y_0z$, a molecular volume associated with each bond.

If e^{-ar} is eliminated between equations (2) and (3), the result can be written as

$$F^* = \tfrac{1}{2}F_0^*(1 + 2\lambda f + \sqrt{1 - 4\lambda f}) \tag{4}$$

where $\lambda = v/2anF_0^*$.

For small stresses, equation (4) when expanded gives

$$F^* = F_0^*(1 - \lambda^2f^2 - 2\lambda^3f^3 - 5\lambda^4f^4 - \cdots) \tag{5}$$

which shows that, to a first approximation, F^* is not a linear function of the stress but a quadratic one.

Now that the form of the force/energy curve has been derived, its application to the effect of stress on a solid can be considered. A "chain" of bonds from atom to atom can always be drawn approximately in the direction in which deformation takes place and, in this sense, all solids are long-chain polymers, the usual term being applied to molecular chains of covalently linked atoms. In general, some of the bonds along the "chain" will be much weaker than covalencies, e.g., hydrogen bonds or van der Waals forces, and it will be these which are most greatly deformed when their particular "chain" of bonds is under stress. Where a weak bond occurs in parallel with a chain of strong bonds, the latter will carry the load and transfer it to some other weak bond not flanked by inextensible bonds. In this way, only a certain critical fraction of the weak bonds will be responsible for the whole of the elastic deformation and their rupture under the stress concentrated on them can be the source of the viscous or plastic properties of the material. Efforts to calculate the magnitude of the modulus and breaking strength of a material from its primary chemical structure may thus be in vain if it is the relatively weak, secondary bonds, and not the main valence bonds, which are more important. The extension of the covalent bonds, because of their high energy, is likely to be completely negligible at the low stresses applied, and the previous equations will therefore refer solely to the deformation of the critical weak bonds.

Although the weak bond under stress is extended by a fraction r, the material as a whole will be stretched to a smaller extent depending on the length in which, on the average, one weak bond occurs. If the ratio of this length to the equilibrium bond length is q then the actual extension per unit length, ϵ, is related to r by the equation

$$\epsilon = r/q \tag{6}$$

Since Young's modulus E is $(\partial f/\partial \epsilon)_{f=0}$ it follows, by differentiating equations (3) and (6), that

$$E = \frac{2a^2F_0^*}{nv}q \tag{7}$$

$$= aq/\lambda \tag{8}$$

The coefficient λ which determines the magnitude of the influence of stress on the activation energy could thus be calculated from the elastic modulus provided

that the molecular parameters a and q were known. But if the material exhibits a clearly defined yield point, even these need not be known since λ can be expressed in terms of the experimentally observable modulus E and the yield extension ϵ^* as follows: By differentiating equation (3), the maximum stress on each bond can be shown to occur when $ar = \ln 2$ and this, substituted in equation (6), gives

$$\epsilon^* = \ln 2/aq \tag{9}$$

whence

$$\lambda = \ln 2/E\epsilon^* \tag{10}$$

Equation (3) can thus be put in the form:

$$f = 1.4426E\epsilon^*(2^{-\epsilon/\epsilon^*} - 2^{-2\epsilon/\epsilon^*}) \tag{11}$$

since $1/\ln 2 = 1.4426$. This equation describes a nonlinear spring with a stress-strain curve having the shape shown in Figure 1.

The curves show that, for a given stress, there are two possible values for the extension. The short form is a stable state, but the longer one is unstable. To pass from the short to the longer form, the atoms constituting the bond must absorb energy from their surroundings.

This is in harmony with the phenomenon of cooling on stretching which occurs with normal elastic bodies where internal energy is the major factor in contrast with the heating which occurs on stretching rubberlike materials where entropy changes predominate. The difference in energy between the long and short states (ΔF^*) can be derived from equation (4) and is given by:

$$\Delta F^* = F_0^*\sqrt{1 - 4\lambda f} \tag{12}$$

For small values of f, equation (12) can be expanded to give

$$\Delta F^* = F_0^*(1 - 2\lambda f - 2\lambda^2 f^2 - 4\lambda^3 f^3 - \cdots) \tag{13}$$

which, to a first approximation, is similar to equation (1) if $2\lambda F_0^*/kT = a$.

As the stress is increased, a maximum is approached at which $\epsilon = \epsilon^*$, beyond which the weak bond breaks. When each bond breaks a segment of the "chain" is free to straighten out until another weak bond comes under strain, and the process continues, giving the effect of plastic flow until the material finally breaks.

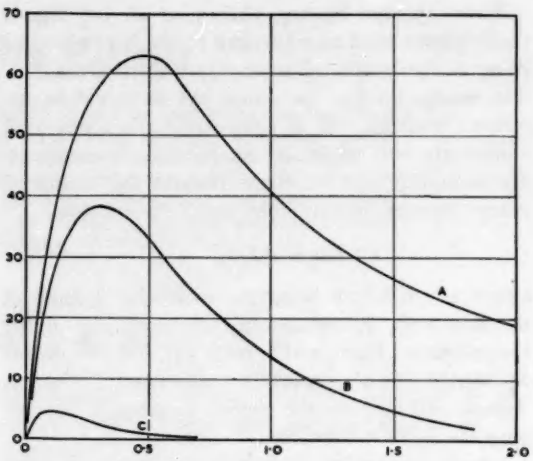

Fig. 1. Stress-strain curves due to deformation of bonds. *A*, Coulombic attraction; *B*, covalent bonds; *C*, van der Waals forces.

Before the maximum point is reached, however, bond rupture will have commenced because of the Maxwell-Boltzmann distribution of thermal energy. According to the Tobolsky-Eyring theory, the rate of bond rupture due to this effect will be of the form

$$\frac{kT}{h}e^{-F^*/kT} = \frac{kT}{h}e^{-F_0^*/kT}e^{\alpha f} \tag{14}$$

in accordance with equation (1). The rate of reformation of bonds was assumed to take a similar form but with a negative exponential stress term. Each bond, when broken, was thought to permit a certain amount of flow and the rate of flow could then be expressed as

$$\frac{d}{dt} = \frac{K}{2}(e^{\alpha f} - e^{-\alpha f}) = K \sin h\alpha f \tag{15}$$

where K involves the distance moved by the freed segments of the chain when the bond is broken.

The present theory also predicts that the form of the bond-breaking reaction should be similar to equation (14) for small stresses if ΔF^* is the true activation energy barrier; otherwise equation (4) should hold and for small stresses the quadratic form of (5) is correct. For the bond re-formation reaction, however, difficulties immediately emerge. The Morse equation shows that stress can reduce the activation energy barrier but gives no indication that it could *increase* it as in the Tobolsky-Eyring postulate. It

therefore seems reasonable to assume that there is little or no stress on the broken bonds; they have transferred the stress to some other weak bonds not previously affected. Where groups of several weak bonds occur in series with one another, all simultaneously under stress, they will behave as a spring of low modulus in parallel with those chains having few bonds and which therefore take most of the strain. Such parallel chains in which the bonds do not break provide a tendency to recover the original configuration (elasticity).

The broken bonds produce free valencies (radicals) which may combine with other atoms (water molecules in the atmosphere, or similarly freed bonds from other "chains," for example) and thus fall into another potential energy well which would delay bond re-formation into the original configuration. This reaction leads to viscous behavior or, in the extreme case, permanent set. An attempt to apply part of this theory to the rheology of paper has already been made [4], but it is hoped that elsewhere will be developed the particular theory applicable to the viscoelasticity of keratin fibers. The general principle, however, should be applicable to the problem of fatigue in textile or other materials, to stress-activated reactions, or any such mechanochemical phenomena.

Summary

A new approach to the theory of viscoelasticity of solids is developed. The novel feature is the attempt to established a connection between the bond energy (F_0^*) and the elastic modulus of elongation (E), the yield strain (ϵ^*), and a viscous coefficient of flow λ. To do this, nothing more is used than the well-known properties of chemical valence-bonds together with a view of solids as polymolecular or atomic "chains" of bonds, in series and in parallel, some bonds having lower bond energies than the others. The effect predicted by this model is that of a nonlinear spring in series with a dashpot having a nonlinear viscosity, both in parallel with a similar nonlinear spring of lower modulus.

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L. PETERS

Fiber Blending

COURTAULDS (ALABAMA) INC.
Mobile, Alabama

December 29, 1954

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Messrs. Coplan and Klein, of Fabric Research Laboratories, Inc., have been kind enough to point out to me an error in the argument in the section, "The Perfect Blend," in my paper, "Fiber Blending," published in TEXTILE RESEARCH JOURNAL, Volume XXIV, No. 8, August 1954.

In that paper, I likened a 20's yarn of 50% black and 50% white fibers to two 40's yarns, one black and the other white, each having a best regularity calculable from the equation

$$(CV)^2 = \frac{100^2}{n} + \frac{(CV_f)^2}{n}$$

I suggested that, where one component may be dissolved out of the yarn by chemical means, the

degree of regularity of the remaining component may be determined, and that, according to this general concept,

$$(CV_A)^2 = \frac{100^2}{n_A} + \frac{(CV_{fA})^2}{n_A}$$

and

$$(CV_B)^2 = \frac{100^2}{n_B} + \frac{(CV_{fB})^2}{n_B}$$

Here CV_A and CV_B are the coefficients of variation of the weight per unit length of fiber A and fiber B along the yarn, and CV_{fA} and CV_{fB} are the coefficients of variation of individual fiber weights per unit length of the two components. The two latter terms are quite small and may, for all practical purposes, be ignored.

I also suggested that, since, from the theory of analysis of variance

$$CV^2 = (CV_A)^2 + (CV_B)^2 = 100^2\left(\frac{1}{n_A} + \frac{1}{n_B}\right)$$

it is possible, knowing the coefficient of variation of the yarn within a given length and the coefficient of variation of fiber A after dissolving out fiber B, to calculate the coefficient of variation of fiber B.

The general line of thought is still correct, but, as has been pointed out to me by Coplan and Klein, the expression

$$CV^2 = 100^2\left(\frac{1}{n_A} + \frac{1}{n_B}\right)$$

should not be used for this calculation since, according to the earlier part of this concept

$$(CV)^2 = \frac{100^2}{n}$$

$$(CV_A)^2 = \frac{100^2}{n_A}$$

and

$$(CV_B)^2 = \frac{100^2}{n_B}$$

and, by definition, $n = n_A + n_B$, then

$$\frac{100^2}{n} \neq \frac{100^2}{n_A} + \frac{100^2}{n_B}$$

and

$$\frac{1}{n} \neq \frac{1}{n_A} + \frac{1}{n_B}$$

The corrected version appears to be as follows: Since, by definition,

$$n = n_A + n_B$$

and

$$CV^2 = \frac{100^2}{n}$$

$$CV^2 = \frac{100^2}{n_A + n_B} \quad \text{and} \quad \frac{1}{CV^2} = \frac{n_A + n_B}{100^2}$$

and so the expression used should be

$$\frac{1}{CV^2} = \frac{1}{CV_A{}^2} + \frac{1}{CV_B{}^2}$$

and

$$(CV)^2 = \frac{100^2}{\left[\dfrac{\text{Cotton count fiber (fiber fineness) } A}{\text{Equivalent cotton count } A \text{ as yarn}} + \dfrac{\text{Cotton count fiber } B}{\text{Equivalent cotton count } B \text{ as yarn}}\right]} \tag{5}$$

The general conclusions drawn are unchanged.

G. V. LUND

INDUSTRIAL SECTION

A Method of Calculating Theoretical Fineness for Cotton Blends

Edwin J. Jennings and Henry G. Lewis[1]

Introduction

Fiber fineness has become a major factor in merchandising cotton and in manufacturing cotton products. Mills often specify a desired range of Micronaire readings. In processing the cotton they sometimes find that the Micronaire reading of a blend is not the arithmetic mean of the individual Micronaire readings of the bales used in the mix. In this paper an explanation of this apparent discrepancy is presented, and also a difficulty encountered in Micronairing two-sided bales is mentioned.

Discussion

The fineness of cotton fibers is expressed in terms of a unit such as micrograms per inch (μg/in.); therefore when one is calculating the average of several values of fineness, he must take care how each value is weighted. If fineness is weighted on the basis of length, then an arithmetic mean gives the theoretical fineness for the blend. For example, a blend of two 1-in. fibers whose finenesses are 3 and 6 μg/in. would weigh 9 μg. Since the total length is 2 in., the fineness of the blend is 4.5 μg/in., which is the arithmetic mean of 3 and 6. If, however, equal *weights* of these two cottons were blended, there would be twice as many fine fibers as coarse ones. For example, a blend of 6 μg of each of the above cottons would contain one coarse fiber and two fine ones. The total weight would be 12 μg, the total length, 3 in., and the fineness of the blend would be 4.0 μg/in., which is the harmonic mean of 3 and 6. Therefore, if a blend is made on the basis of weight —which is usually the case—the harmonic mean should be used to calculate its theoretical fineness.

[1] This study was made in the ACCO Fiber and Spinning Laboratory, Anderson, Clayton & Co., Houston, Texas, under the direction of Earl E. Berkley.

In the second example above, 6 μg of one cotton was blended with 6 μg of another; however, if the amounts are different, a "weighted" harmonic mean must be used. A general formula for calculating the "weighted" harmonic mean—which is the theoretical fineness of a blend—for any combination of any number of individual components is as follows:

$$F_b = \frac{W_t}{\frac{W_1}{F_1} + \frac{W_2}{F_2} + \cdots + \frac{W_n}{F_n}} = \frac{W_t}{\sum \frac{W}{F}} \qquad (1)$$

where F_b is the fineness of a blend of n components; W_t is the total weight of the blend; and W is the weight of any one component and F is its fineness. In terms of weight percentages this equation would be:

$$F_b = \frac{100}{\frac{P_1}{F_1} + \frac{P_2}{F_2} + \cdots + \frac{P_n}{F_n}} = \frac{100}{\sum \frac{P}{F}} \qquad (2)$$

where P is the percentage by weight of any one component and F is its fineness. If *equal* weights of the individual components are blended, the general formulas above may be simplified somewhat, and, as a special case:

$$F_b' = \frac{n}{\frac{1}{F_1} + \frac{1}{F_2} + \cdots + \frac{1}{F_n}} = \frac{n}{\sum \frac{1}{F}} \qquad (3)$$

where F_b' is the fineness of a blend of equal amounts by weight of n components, and F is the fineness of any one component.

The harmonic mean of two or more different fineness values is always less than the arithmetic mean; however, when the fineness values do not differ widely, the arithmetic mean is a good approxima-

tion of the harmonic mean. In making numerous calculations of harmonic means, it is expedient to have available a table of reciprocals.

When Micronaire determinations are made on Upland samples using the curvilinear scale calibrated for American Upland cottons—which is the scale most frequently employed—the Micronaire reading is an approximation of the micrograms per inch; hence the Micronaire reading of a blend may be estimated from the Micronaire readings of the individual bales according to the above formulas (1), (2), and (3).

Equal amounts of five samples having Micronaire readings of 2.3, 3.3, 4.8, 5.5, and 6.5 were blended in a fiber blender, and the average Micronaire reading for the blend was 3.95. Equal quantities of the same five samples were then carded after blending, and the average Micronaire reading for the card web was 3.95 also. The harmonic mean of the individual Micronaire readings is 3.90; whereas the arithmetic mean is 4.48. The observed averages of 3.95 agree quite well with the harmonic mean, but not the arithmetic mean.

One cotton having a Micronaire reading of 2.3 was mixed in various proportions with another cotton having a Micronaire reading of 6.5. Micronaire determinations were made on each of these "poor blends," thereby assimilating conditions when testing a two-sided bale by making only one determination. These mixtures, or "poor blends," were then blended in a fiber blender, and Micronaire readings were determined again. These same samples were then carded, and Micronaire readings were again taken on the card web. This procedure was repeated twice, and the averages for the three runs were calculated. These data are presented in Table I together with the harmonic means as calculated from the general formula (2) above. The arithmetic means are also listed for comparison. (The harmonic means and the arithmetic means were calculated using 2.3 as the Micronaire reading for the fine cotton and 6.5 for the coarse one, since these values

TABLE I

Fine Cotton (%)	Coarse Cotton (%)	Poorly Blended					Well Blended				
		Run 1	Run 2	Run 3	Mean	σ*	Run 1	Run 2	Run 3	Mean	σ*
0	100	6.5	6.5	6.6	6.5	0.05	6.4	6.6	6.6	6.5	0.09
10	90	6.4	4.6	4.7	5.2	0.83	5.5	5.3	5.2	5.3	0.12
20	80	4.4	5.9	4.6	5.0	0.66	4.5	5.0	4.7	4.7	0.20
30	70	4.4	3.7	3.1	3.7	0.53	4.1	3.9	3.7	3.9	0.16
40	60	3.8	4.1	2.7	3.5	0.60	3.5	3.6	3.8	3.6	0.12
50	50	3.0	3.6	3.4	3.3	0.25	3.4	3.2	3.4	3.3	0.09
60	40	2.8	3.9	2.6	3.1	0.57	2.9	2.9	3.0	2.9	0.05
70	30	2.6	3.0	3.3	3.0	0.29	2.8	2.7	2.8	2.8	0.05
80	20	2.4	2.4	2.4	2.4	0.00	2.5	2.6	2.6	2.6	0.05
90	10	2.5	2.4	2.5	2.5	0.05	2.4	2.5	2.4	2.4	0.05
100	0	2.3	2.3	2.3	2.3	0.00	2.3	2.4	2.3	2.3	0.05
					Mean σ	0.36				Mean σ	0.09

Fine Cotton (%)	Coarse Cotton (%)	Carded					Harmonic Mean	Arithmetic Mean
		Run 1	Run 2	Run 3	Mean	σ*		
0	100	6.1	6.3	6.3	6.2	0.14	6.5	6.5
10	90	5.3	5.3	5.8	5.5	0.24	5.5	6.1
20	80	5.1	4.4	4.6	4.7	0.29	4.8	5.7
30	70	4.2	4.0	4.2	4.1	0.09	4.2	5.2
40	60	3.8	3.8	3.7	3.8	0.05	3.8	4.8
50	50	3.5	3.4	3.4	3.4	0.05	3.4	4.4
60	40	3.0	3.1	3.0	3.0	0.05	3.1	4.0
70	30	2.9	2.8	2.8	2.8	0.05	2.9	3.6
80	20	2.7	3.0	2.7	2.8	0.14	2.6	3.1
90	10	2.5	2.5	2.5	2.5	0.00	2.5	2.7
100	0	2.3	2.4	2.3	2.3	0.05	2.3	2.3
					Mean σ	0.10		

* Standard deviation.

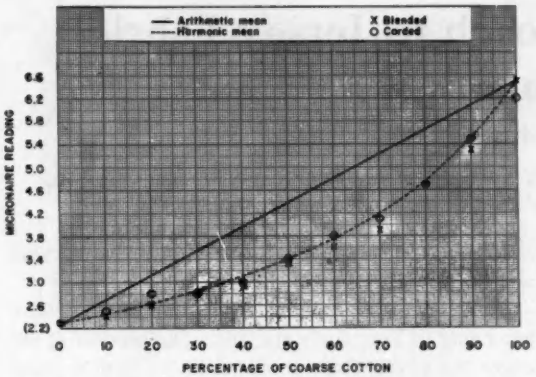

Fig. 1. Averages of the three runs compared with harmonic and arithmetic means for the 2.3–6.5 blend.

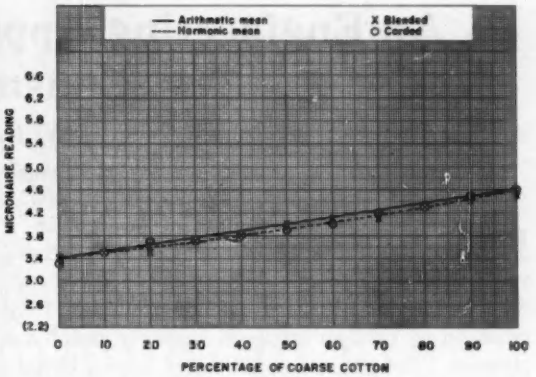

Fig. 2. Averages of the three runs compared with harmonic and arithmetic means for the 3.4–4.6 blend.

were the averages of three runs on the raw stock as shown in Table I under the "poorly blended" series.) The averages of the three runs are graphically compared with the harmonic and arithmetic means in Figure 1.

Six other similar tests were made using cotton with the following Micronaire readings:

	Fine	Coarse
a	2.4	5.5
b	2.4	4.8
c	2.3	3.3
d	3.4	6.2
e	3.3	5.4
f	3.4	4.6

The same general relationships were observed; and, as mentioned above, the difference between the harmonic and arithmetic means decreased as the Micronaire readings of the two cottons used in the blend approached one another. This is shown graphically in Figure 2, which represents data from the 3.4–4.6 blend listed above.

From these seven tests it was evident that the average standard deviation for the "poorly blended" series was much larger than those for the "well blended" and the carded ones. This reflects the larger variation between individual runs for the "poorly blended" case and indicates the perplexities to be expected when Micronairing two-sided bales if only one determination per bale is made on an unblended sample.

In the routine testing of samples from certain areas it is necessary to consider the problem created by two-sided bales. Reliable data may be obtained either from one test on a blended sample or from two tests, one on each side of the bale. It is more economical to make one test on each side than to blend the two sides and make one determination on the blend. In calculating the average Micronaire reading, it is recommended that a harmonic mean be used if the difference in the two sides is 1.0 Micronaire unit or greater. If the difference is less than 1.0, an arithmetic mean is usually satisfactory for routine testing; however, for precise measurement—such as used when comparing results of several laboratories—a harmonic mean should always be used.

Revised manuscript received October 28, 1954.

An Engineering Approach to Jersey Fabric Construction[1]

W. E. Shinn

Head, Department of Knitting Technology, North Carolina State College, Raleigh, North Carolina, and Research Consultant for the Underwear Institute

KNITTING had its beginning as an art. Fabrics and articles of clothing were first fashioned by hand. Skill and manual dexterity of the craftsman were relied on to yield an article to supply a useful end purpose. The production of knitted fabrics by machines has been practiced more than 350 years, but still a great number of the textiles produced on knitting machines involve art and skill to a high degree.

Arts cease to be arts and evolve as sciences where measurement comes to be relied upon, when laws of cause and effect are discovered, defined, and stated so that others who follow may achieve the same results. In engineering practice one must be able to plan and predict with reasonable assurance that the end product will be as it was planned.

The author's purpose in this paper is to treat knitting not as an art but as a science. This discussion of the engineering approach is concerned with some of the fundamental laws of knitting: with measurement; with calculations; and with prediction. It is limited to the simplest of all knit structures, the jersey or plain fabric, also called flat fabric. This structure is the most common and is found in many of the apparel fabrics. It is found in some of the heavier articles of knitted clothing and in the sheerest hosiery fabrics, although the treatment herein is from the viewpoint of apparel fabrics in which good body and shape retention qualities are of great importance.

The jersey fabric is made on a single bank of needles, and all the stitches are drawn in the same direction (back to face). Assuming that the needles are operating continuously, the character of this fabric is determined almost entirely by the yarn itself. The machine determines the length of stitch, but beyond this the qualities possessed by the fabric are fixed by the yarn itself. Jersey fabric is built of loops or stitches aligned in vertical rows or wales, and horizontal rows called courses.

These loops on being formed into fabric behave according to Tompkin's law [3]: *The product of the wales and courses with a given stitch length is equal to a constant* (Figure 1).

We may demonstrate this law by assuming that a knitting machine is producing a fabric with 10 wales and 10 courses per inch. The product is obviously 100. If we change to a lighter yarn so that the wales per inch are increased to 11, the courses will automatically become 9.09, and the product will remain unchanged at 100.

The weight per unit area is thus proportional to the weight per unit length of the yarn used or inversely proportional to the cotton yarn numbers. This may be stated as follows:

$$\frac{\text{wt. } 1}{\text{wt. } 2} = \frac{\text{No. } 2}{\text{No. } 1} \qquad (1)$$

This formula may be used to predict the change in fabric weight which will be caused by changing from one yarn size to another, or to determine the yarn count required to yield a desired fabric weight on the same machine with the same setting of the cams.

The wales per inch are determined by the yarn diameter. Each wale is approximately equal to 4 yarn thicknesses. This is true because the knitted structure tends to close in width and becomes stable when the side of the loops are flush with one another. The spacing of the needles does not fix the spacing of the wales because it is possible to make a variety of fabrics on the same machine merely by exchanging one yarn for another.

The Law of Amplification

Small differences in yarn diameter are magnified by the knitting process. Because the width of each wale is determined by four yarn thicknesses, differences in yarn thickness are multiplied by the factor 4 in each needle wale. This is the law of amplifica-

[1] Presented at a symposium on knit fabric structures at Massachusetts Institute of Technology held in connection with the MIT Summer Program, "Applied Mechanics of Textile Structures."

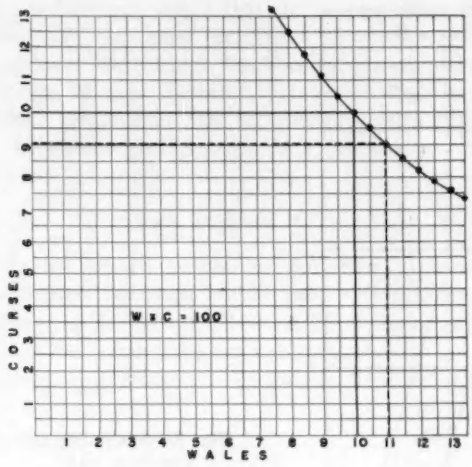

Fig. 1. Wale-course ratio, Tompkins' law.

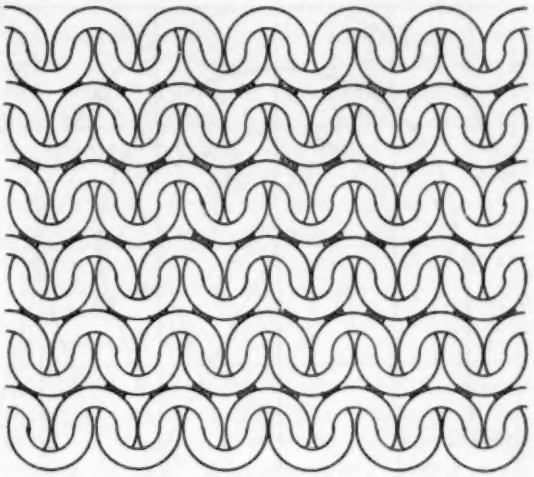

Fig. 2. Plain jersey, back view.

tion and may be stated as follows: *Differences in yarn diameter are amplified on the knitting machine by a factor equal to four times the number of needles in the machine.* This means that a difference of 1 mil in yarn diameter will result in a 4-in. difference in the width of fabric produced by 1000 needles. Because the knitting machine does magnify small difference in yarn thickness, its use as a testing instrument for the measurement of yarn diameter suggests itself.

It has been stated above that the loops form a stable structure when they contract in width and touch one another. Is there a stable position for the loops in a vertical direction? Figure 2 shows a view of the jersey structure as seen from the back. This stitch is drawn in what we choose to call a normal stitch. The needle loops are seen to be essentially in contact with the sinker loops in the next course. The jersey stitch is frequently made longer than this, but the author's concern here is with apparel fabrics as opposed to sheer constructions such as women's hosiery.

Figure 2 shows that, while 6 wales and 6 courses have been illustrated, the area is not a square but is wider than it is high. Dividing the width by the depth we obtain a factor of 1.15, which is the normal ratio of courses to wales. In this fabric the stitches are said to be in equilibrium. Any attempt to finish this fabric as a square is likely to produce temporary results. To see why this is true, see Figure 3, a drawing of one complete loop of jersey fabric. The scale used is unity. The stitch has been drawn to cover 4 squares in the diagram since its width is equal to 4 yarn diameters. The length of the loop may be calculated by computing the length of the center line or axis of the yarn.

Computing the Stitch Length in Jersey Fabric in Terms of the Yarn Diameter

Let d, the yarn diameter, be equal to unity. Then one stitch or unit cell will be equal in width to $4d$ because of the stitch structure. If the stitch length be shortened sufficiently, then the sinker loops in one course will become tangent with the needle loops in the consecutive course.

Figure 3 illustrates the jersey stitch for yarn having a diameter of unity. The complete stitch is composed of an upright loop and an inverted loop, the axis of which is described by the arc AB, the straight line BB', another arc $B'D$, and the straight line DE.

The length of this line is computed as follows: Considering the right triangle GOB:

$$\cos GOB = \frac{1.5}{2} = 0.75$$

$$GOB = 41^\circ 25' \quad \text{also} \quad B'O'G = 41^\circ 25'$$

Then: $FO'B' = 60^\circ - 47^\circ 25' = 18^\circ 35'$

The degrees in the arc BD are then:

$$180^\circ + 2(18^\circ 35') = 217^\circ 10'$$

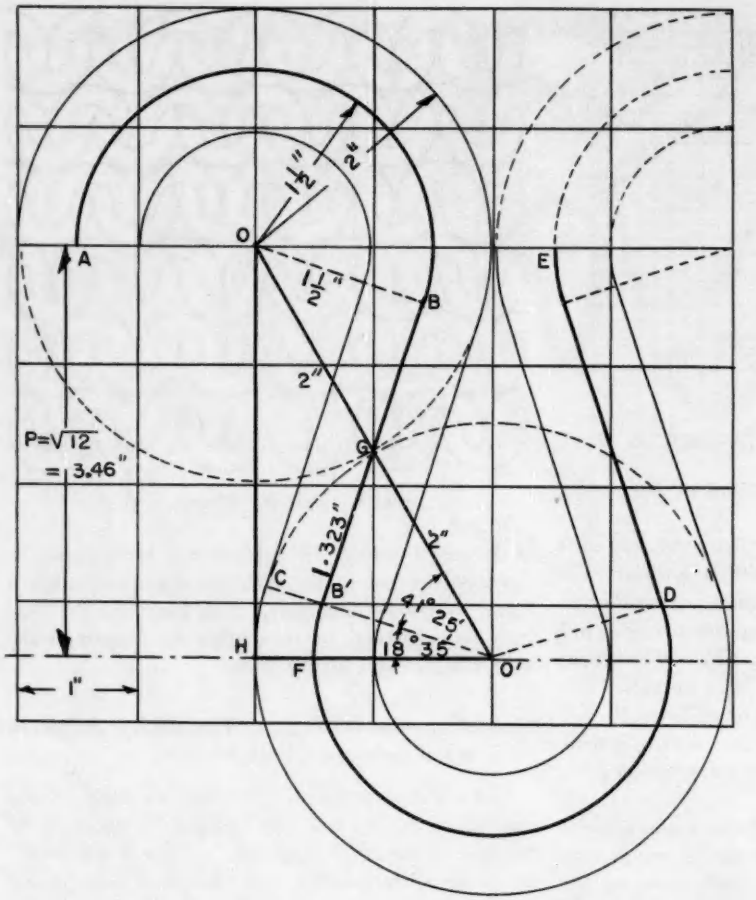

Fig. 3. Stitch diagram, geometric view.

Since an equivalent arc AB forms the upright needle loop, the total is $2(217° 10') = 434° 20'$.

The length of these two elements is:

$$\frac{3\pi \times 434° 20'}{360°} = 11.37 \text{ units}$$

The length of side $B'G$ of right triangle $O'B'G$ is:

$$\sqrt{2^2 - 1.5^2} = \sqrt{1.75} = 1.323 \text{ units}$$

but there are four of these elements in one complete stitch

$\therefore$ $4 \times 1.323 = 5.29$ straight-line portions of the stitch

$11.37 + 5.29 = 16.66$ units, length of one stitch

Computing the Stitch Height

The height of the stitch is represented by the line OH in Figure 3. This line is a side of the right triangle $O'HO$. $OG = 2$ in. $OO' = 4$ in.

$$\therefore \quad OH = \sqrt{4^2 - 2^2} = \sqrt{12} = 3.4643$$

The width of the stitch is 4; therefore the normal relationship between the width of the stitch and its height is 4 to 3.4643, or 1.15.

$$\frac{C}{W} = 1.15 \qquad (2)$$

Using this ratio as a basis for calculation, it is thus possible to determine that a jersey fabric with 26 wales per inch should be knitted with 30 courses per inch.

The stitch drawing is essentially the same as that used by Peirce [2] except that the author has chosen to treat the stitch as though it lay entirely in the same plane. While this is not exactly the

case, it has been found that the plane-surface distances give very good correlation in practice. The formula for stitch length has been expressed entirely in terms of yarn diameter. Here we might state another fundamental law of knitting: *Stitch length in the normal jersey fabric is a function of yarn diameter.*

$$\text{Stitch length} = 16.66d \qquad (3)$$

The spacing of the needles and other mechanical factors have been ignored because it is possible to duplicate a fabric knitted on a 12-cut machine by placing the same yarn on a 14-cut machine or by hand knitting where the machine is dispensed with.

Testing the Formula

A series of nine plain fabrics were knitted, using yarns from 4/1 to 30/1. The knitting machines were adjusted to knit with the normal stitch, $L = 16.66d$. The object of these tests was to determine the wale/course ratios of the fabrics knitted with normal stitch. The test fabrics were finished to yield actual wale counts equal to the theoretical wales per inch for each yarn. In this condition the courses were counted. The ratios are listed in Table I. The values for 8 yarns have been plotted and are shown graphically in Figure 4. There is good correlation with the expected ratio 1.15. The diagonal line represents theoretical values of the 1.15 ratio between courses and wales.

TABLE I. Course-Wale Ratios in Several Jersey Fabrics Knitted with Normal Stitch

Yarn No.	Wales per Inch	Courses per Inch	Ratio $C \div W$	Actual Stitch Length L	Calc. Stitch Length
4	12	14	1.17	0.340	0.345
6	14.2	16	1.13	.290	.283
8	17	21	1.23	.245	.242
10	19.5	22	1.13	.215	.216
12	21	23½	1.12	.190	.199
15	23.5	27	1.15	.178	.175
21	27.5	32	1.16	.158	.150
25	31	36	1.16	.130	.133
30	33	38	1.15	.122	.125

Yarn Diameter and Density

Refer to Figure 5. A value of 0.67 specific density for cotton knitting yarn was used in this study. A value higher than this has been used by other writers and experimenters, but in most cases, reference was made to weaving yarns which are harder twisted and more dense than knitting yarns. Number 10 yarn is assumed thus to have a diameter of 13 mils, and it was demonstrated that this yarn yielded a fabric with 19.25 wales and 22 courses, thus satisfying the equation:

$$\text{Wales per inch} = \frac{1}{4d} \qquad (4)$$

$$19.25 = \frac{1}{4 \times 0.013}$$

The diameter of yarns having a density of 0.67 may be calculated by use of the following formula:

$$D = \frac{1}{24\sqrt{\text{No.}}}$$

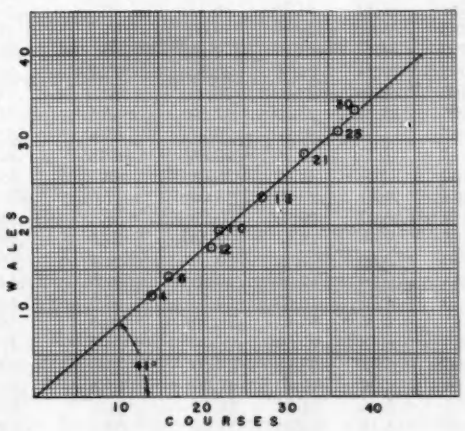

Fig. 4. Course-wale ratios, chart.

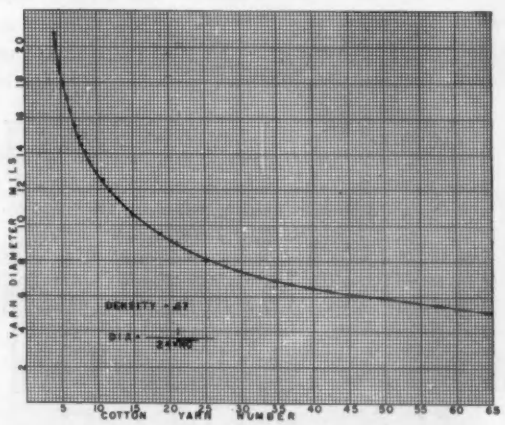

Fig. 5. Yarn diameter vs. yarn number.

Fabric Width

The author was recently asked to supply a table showing the correct widths to which fabrics should be finished from various sizes of knitting machines. There is no fixed relationship between cylinder diameter and the tubular width of the fabric, because it is possible to make fabrics in several different widths on the same knitting machine by changing yarns and possibly altering the stitch length. It is, however, a matter of coincidence that the width of the fabric in flat tubular form is about the same as the diameter of the machine cylinder upon which the fabric was knitted. Fabric width is a function of the yarn diameter, and the total number of needles used in its formation (Figure 6).

In this chart yarn diameter is shown on the vertical scale, and the width of the tubular fabric in inches for 1000 needles on the horizontal scale. Note that, in constructing this chart, cylinder diameter and needle spacing have not been included.

Shrinkage

A great deal has been written recently about fabric shrinkage. A leading technologist in the knitting industry when asked the question, "What is the most pressing problem in knitwear manufacture?" replied, "Shrinkage control." Many are the reports that garments made of jersey fabric do not hold their shape and as a result lose their serviceability. This experience could better be described as fabric distortion because our studies on the cotton yarns used in knitting do not reveal any great amount of shrinkage in the yarns themselves. Fletcher and Roberts [1] reported the same experience in their investigations in knitted fabric construction and shrinkage. If the yarn does not shrink, then where does this shrinkage originate?

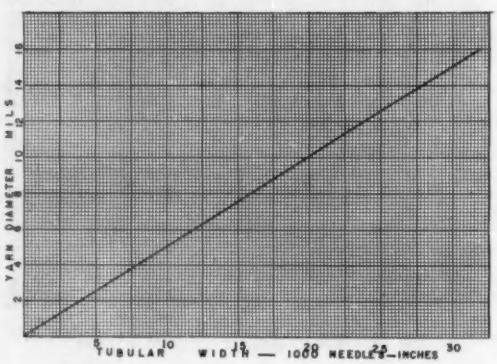

Fig. 6. Yarn diameter vs. tubular width.

The indications are that much of the reduction in length which the customer experiences with his knit garments is gained in the width, so that the total area is still about the same. Better equipment has been produced for finishing knitted fabric, and this is doing much to improve quality, but even with the minimum equipment the average producer would make a better product were the laws of knitting better understood and observed.

Predicting Fabric Weight

We have set up as one of our objectives the prediction of several fabric properties. One of the most difficult of these to predict is the weight per square yard. Tompkins [3] suggested the following methods:

$$18.987 \times \text{diameter} = \text{wt./sq yd (lb)} \qquad (5)$$

also

$$\frac{0.904}{\sqrt{\text{No.}}} = \text{wt./sq yd (lb)} \qquad (6)$$

In formula (5), Tompkins relies entirely on the yarn diameter, which for fine yarns is difficult to ascertain with a high degree of accuracy. In expression (6), the number alone is used, thus ignoring

TABLE II. Normal Jersey Fabric Constructions

Yarn Dia.	No.	Wales	Courses	Stitches/Ft	Wt./Yd²
0.0055	57.39	45.45	52.45	131	0.1635
.0060	48.22	41.67	48.16	120	.1783
.0065	41.09	38.40	44.31	110	.1932
.0070	35.43	35.71	41.28	103	.2080
.0075	30.86	33.33	38.43	96	.2229
.0080	27.12	31.25	36.13	90	.2378
.0085	24.02	29.40	34.00	84.7	.2526
.0090	21.43	27.77	32.11	80	.2675
.0095	19.24	26.30	30.30	75.7	.2823
.0100	17.36	25.00	28.90	72	.2972
.0105	15.74	23.80	27.50	68.5	.3121
.0110	14.34	22.70	26.27	65.4	.3269
.0115	13.13	21.70	25.04	62.6	.3418
.0120	12.05	20.80	24.08	60	.3566
.0125	11.11	20.00	23.00	57.6	.3715
.0130	10.27	19.23	22.23	55.3	.3864
.0135	9.56	18.51	21.36	53.3	.4012
.0140	8.86	17.80	20.50	51.4	.4161
.0145	8.26	17.24	19.80	49.6	.4309
.0150	7.71	16.60	19.20	48.0	.4458
.0155	7.23	16.12	18.50	46.4	.4607
.0160	6.78	15.60	18.00	45.0	.4755
.0165	6.38	15.15	12.50	43.6	.4904
.0170	6.00	14.70	17.00	42.3	.5052
.0175	5.66	14.28	16.48	41.1	.5201
.0180	5.36	13.80	15.87	40.0	.5350
.0185	5.07	13.51	15.60	38.9	.5498
.0190	4.81	13.15	15.18	37.8	.5646
.0207	4.06	12.07	14.00	34.7	.6152

TABLE III. Summary of Knitting Tests

Yarn No.	Dia.	Wales/In. Calc.	Wales/In. Actual	Courses/In. Calc.	Courses/In. Actual	Ratio C/W	L	Wt./Yd² Calc.	Wt./Yd² Actual
4	0.0207	12.07	12	14	14	1.17	0.3448	0.615	0.624
6	.0170	14.70	14.2	17	16	1.13	.2832	.505	.522
8	.0145	17.24	17	19.8	21	1.23	.2416	.430	.430
10	.0130	19.23	19.5	22.23	22	1.13	.2166	.386	.393
12	.0120	20.8	21	24.08	23.5	1.12	.1992	.357	.341
15	.0105	23.8	23.5	27.5	27	1.14	.1749	.312	.325
21	.0090	27.7	27.5	32.11	32	1.16	.1499	.268	.275
30	.0075	33.3	33	38.43	38	1.15	.1249	.223	.222

diameter, which is an important factor in determining fabric density. In the formula below both diameter and number are used, and it is believed that the combination dN is capable of giving more accurate results in practice.

$$\text{wt.} = \frac{1296 \times L}{W \times C \times 36 \times 840 \times N} = \text{lb}$$

where: wt. = pounds per square yard; 1296 = square inches in 1 sq yd; L = stitch length in inches; W = width of 1 wale; C = depth of 1 course; 36 = inches in 1 yd; 840 = yards in 1 hank; N = cotton yarn number.

By definition: $L = 16.66d$; $W = 4d$; $C = 3.46d$. Substituting in the formula, we have

$$\text{wt.} = \frac{1296 \times 16.66d}{4d \times 3.46d \times 36 \times 840 \times N}$$

or

$$\text{wt.} = \frac{0.05159}{dN} \text{ lb} \qquad (7)$$

Applying formula (7) to the data in Table II, we are able to predict the weight per square yard of the fabric which will be yielded by any given yarn.

Number 10 yarn has a diameter of 13 mils and an expected fabric weight of:

$$\frac{0.05159}{0.013 \times 10} = 0.396 \text{ lb/sq yd}$$

Test samples were knitted from the following yarns: 4/1, 6/1, 8/1, 10/1, 12/1, 15/1, 21/1, and 30/1. The results of these tests are recorded in Table III. Satisfactory correlation was obtained between the theoretical and actual data.

The data have been plotted in Figure 7 to show the relationships of yarn diameter, wales, courses, stitches per foot of yarn, and fabric weight. The curves formed by wales per inch and courses per inch are hyperbolas. The weight curve is a straight line, and it is obvious that the slope of this line may be varied and used to predict the weight of fabric from yarns with densities higher or lower than 0.67.

Effect of Stitch Length on Fabric Weight

At the outset the effect of changing yarns on the knitting machine and keeping the stitch length constant was discussed. We come now to consider the behavior of the knitting process when the yarn remains constant and the stitch length is changed. Reducing the stitch length will cause an increase in the weight per square yard. This gain in weight is due to the increase in the number of courses per inch. To increase the courses per inch, it was necessary to shorten the stitch so that the length of yarn in a course was reduced. The gain from adding courses, however, is greater than the loss incurred through shortening the course, so that the net effect is an increase in fabric weight per square yard. Lengthening the stitch will have the opposite effect.

In the calculations below, the fabric width and wales per inch are assumed to be unchanged:

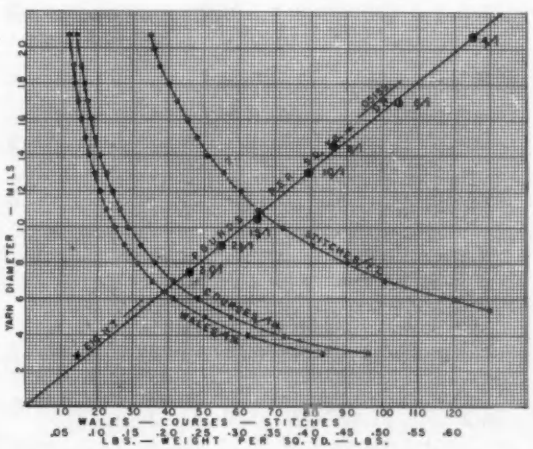

Fig. 7. Yarn diameter, wales, courses, stitches per foot, and fabric weight.

TABLE IV. Effect of Courses per Inch on Fabric Weight 4/1 Cotton Yarn

Fabric No.	Wales, Courses	Weight per Square Yard: Calc. (lb)	Weight per Square Yard: Actual (lb)
1	12×14	0.6240	0.624
2	12×10	.5171	.519
3	12×8	.4636	.459
4	12×6	.4112	.413
5	12×4	.3560	.356
6	12×2	.3034	*
7	12×1	.2767	*
8	12×0	.257 min. wt.	*

* Not knitted.

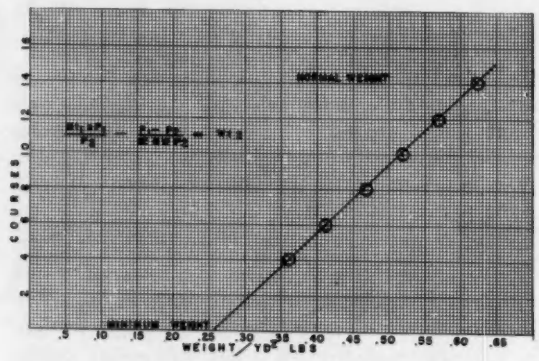

Fig. 8. Effect of courses per inch on fabric weight.

$$\frac{\text{wt. 1}}{36/\text{p. 1}} = \frac{\text{wt. 1 p. 1}}{36} = \text{wt./course old fabric (sq yd basis) (lb)}$$

$$\frac{(72/W)(\text{p. 1} - \text{p. 2})}{36 \times 840 \times N} = \text{loss in wt./course when stitch is shortened.}$$

$$\frac{\text{wt. 1 p. 1}}{36} - \frac{(72/W)(\text{p. 1} - \text{p. 2})}{36 \times 840 \times N} = \text{wt./course new fabric}$$

$$\frac{36}{\text{p. 2}}\left[\frac{\text{wt. 1 p. 1}}{36} - \frac{(72/W)(\text{p. 1} - \text{p. 2})}{36 \times 840 \times N}\right] = \text{wt. 2 sq yd new fabric}$$

$$\frac{36}{\text{p. 2}}\left[\frac{\text{wt. 1 p. 1}}{36} - \frac{(2/W)(\text{p. 1} - \text{p. 2})}{840 \times N}\right] = \text{wt. 2}$$

$$\frac{36\ \text{wt. 1 p. 1}}{36\ \text{p. 2}} - \frac{(72/W)(\text{p. 1} - \text{p. 2})}{840 \times N \times \text{p. 2}} = \text{wt. 2}$$

$$\frac{\text{wt. 1 p. 1}}{\text{p. 2}} - \frac{(1/W)(\text{p. 1} - \text{p. 2})}{11.67 \times N \times \text{p. 2}} = \text{wt. 2}$$

$$\frac{\text{wt. 1 p. 1}}{\text{p. 2}} - \frac{\text{p. 1} - \text{p. 2}}{11.67 \times N \times W \times \text{p. 2}} = \text{wt. 2} \quad (8)$$

where: wt. 1 = wt./sq yd old fabric (lb).
wt. 2 = wt./sq yd new fabric (lb).

TABLE V. Relationship between Yarn Number, Cut, and Stitches per Foot of Yarn for Normal Fabric

Cut = $4\sqrt{\text{No.}}$ No.	Stitches/ft = 4.5 × Cut: Cut	Stitches/ft
1	4.00	18
2	5.65	25.4
4	8.00	36
6	9.80	44
8	11.30	51
10	12.60	58
12	13.85	62
14	14.96	67.3
16	16.00	72
18	16.96	76
20	17.88	80
22	18.76	84
24	19.59	88
26	20.78	93.5
28	21.54	97
30	22.27	100
32	22.62	102
34	23.32	105
36	24.00	108
38	24.65	111
40	25.30	114

TABLE VI. Relation of Fabric Thickness to Yarn Diameter

Yarn Number	Yarn Diameter (in.)	Thickness: Calc. (in.)	Thickness: Actual (in.)
4	0.0207	0.0414	0.0410
6	.0168	.0336	.0395
8	.0145	.0290	.0300
10	.0130	.0260	.0250
12	.0120	.0240	.0225
15	.0105	.0210	.0210
20	.0092	.0184	.0185
25	.0080	.0160	.0170
30	.0075	.0150	.0150

$$\text{p. 1} = \frac{1}{\text{courses/in. old fabric}}.$$

$$\text{p. 2} = \frac{1}{\text{courses/in. new fabric}}.$$

$$W = \frac{1}{\text{wales/in.}}.$$

N = cotton yarn number.

840 = yards in 1 hank.

This formula was tested experimentally on a 10-cut knitting machine with 4/1 yarn. The results are summarized in Table IV and shown graphically in Figure 8. Fabric 1 was knitted with a normal stitch and yielded a fabric with 12 wales and 14 courses. The actual weight of this fabric was 0.624 lb/sq yd. Using formula (8), the weights of the fabric with 10, 8, 6, and 4 courses were calculated.

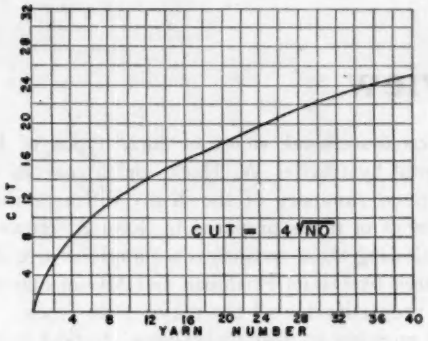

Fig. 9. Yarn number and machine cut.

These fabrics were then produced and found to be approximately the same as the theoretical values in each case. The weight curve, Figure 8, is a straight line and approaches a minimum value of 0.257 lb/sq yd as a limit. This is the value for zero courses, or the weight of unknitted strands of yarn extending through the entire length of the fabric. The number of these parallel strands of yarn is half the diameter per inch for the yarn in question.

The Law of Four-to-One: Yarn-Cut Relationships

We have defined the normal stitch as 16.66 yarn diameters. The wale width has been defined as 4 yarn diameters. In doing this we have established a 4:1 (approx.) relationship between the stitch length and the wale width. This means that in all fabrics knitted with the normal stitch, approximately 4 in. of yarn will be knitted on each course for each inch of fabric width. Normal contraction for jersey fabrics is therefore 75%.

This contraction of the yarn as it is knitted into fabric takes place in two stages. First, the yarn is kinked on the needles. The normal spacing of the needles for each inch of cloth is 1½ in. of needles for each inch of cloth width. Our 4 in. of yarn is therefore first reduced to 1½ in. where it is taken by the needles and knitted into fabric. In the second stage, the fabric closes to 1 in. as it is drawn from the needles. The shrinkage or contraction, yarn to needles, is therefore 62.5%. In the second stage, needles to fabric, the shrinkage is 12.5%.

In setting up the ratio 1½ in. of needles for each inch of fabric width, the needle spacing of the machine, commonly defined as 1/cut, has been fixed at $1\frac{1}{2}W$, the wale width. The wale width has been defined as $4d$; therefore, the needle spacing is equal to $6d$.

$$\text{Cut} = \frac{1}{S} = \frac{1}{6d}$$

or

$$\text{Cut} = \frac{1}{6/(24\sqrt{\text{No.}})}$$

$$\text{Cut} = 4\sqrt{\text{No.}} \qquad (9)$$

This formula has been used in computing the values given in Table V, and these are shown graphically in Figure 9. This table will indicate the normal cut which should be used for each yarn number. This does not mean that each yarn cannot be knitted on some other cut in the same range, but the one shown for each yarn is normal.

The values for stitches per foot of yarn have been computed on the assumption that 4 in. of yarn will be fed to each 1.5 in. of needles, or 12 in. of yarn to each 4.5 in. of needles. The stitches per foot in each case are therefore 4.5 × cut (needles per inch). One foot of yarn is taken as the unit because it is a convenient length for control of the knitting machine. In practice, the yarn should be marked at points 12 in. apart. This section of yarn is then knitted into fabric, and the number of needles or wales lying between the two marks are recorded as the stitches per foot of yarn.

Fabric Thickness

So far we have dealt with the wales and courses which represent two dimensions of the fabric. It is perhaps not always remembered, but fabric has a third dimension, thickness. Can this dimension be predicted from the yarn itself? Tompkins [3] defines *thickness* as equal to two diameters of yarn.

$$T = 2d \text{ (jersey fabric)}$$

Using the above formula the theoretical thicknesses of several experimental fabrics were calculated. The fabrics were later tested for thickness. The theoretical results are compared with the experimental values in Table VI. The closeness with which these two agree indicates that thickness is a function of yarn diameter and is equal to $2d$.

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Manuscript received August 11, 1954.

Book Review

Harris' Handbook of Textile Fibers. Edited by Milton Harris. Published by Harris Research Laboratories, Inc. Washington, D. C., 1954. 356 pages. Price, $12.50.

Reviewed by Helmut Wakeham, Textile Research Institute, Princeton, New Jersey

The ever-expanding literature on textile fibers and the increasing research effort in this field have created a need for reference works in which are compiled the extensive technical data now available on fibrous materials. This need has become acute in recent years with the frequent introduction of new fibers presenting unusual combinations of fiber properties to the textile designer and engineer. Of the several books published to fill this need, this is one of the most complete, and has been prepared by a staff of eminent authorities in the field.

One serious problem in the preparation of a work of this sort is in the selection of material to be included. The user of a handbook would like it to contain only the most reliable and accurate data available, presented in a unified and readily accessible form. Preparation of such a handbook places an almost impossible burden of judgment and responsibility upon the editor. Furthermore, compilation of the heterogeneous data in the textile fiber literature into unified tables employing common units of measure would require a tremendous amount of editorial work. A more practical alternative method of presentation is to reproduce the best and most recent data in the form in which it originally appeared. This method has been employed by the authors of *Harris' Handbook of Textile Fibers.* It has the advantage of permitting the user to compare conveniently results obtained by different workers and to make his own selection without an extensive search of the literature.

The books begins with a glossary of textile terms and definitions. This is followed by a detailed compendium of fiber types and sources including a catalog of manufacturers of man-made fibers, foreign and domestic. Next comes a section on the constitution and structure of fibers. This part contains a collection of excellent photomicrographs of longitudinal and cross-sectional views of forty types of fibers gathered by Charles W. Hock, and a concise, well-illustrated summary of the X-ray diffraction characteristics of fibers prepared by John A. Howsmon.

Following these sections is a comprehensive chart, prepared by Daniel Frishman and Milton Harris, of fiber properties for all the major fiber types. This chart summarizes fiber dimensions, physical and mechanical properties, and chemical reactivities. Recent information on improved Acrilan and Teflon fibers has been included in supplemental tables.

The sections on physical and chemical properties comprise the major portion of the book. Physical properties include dimensional and quality characteristics, specific gravities, mechanical, optical, electrical, thermal, frictional, and air-permeability properties—75 large pages of tables and diagrams taken from the last 25 years of literature on textile material. Chemical properties include sorption and swelling, isoelectric and isoionic points, acid and base binding, dyeing properties, solution viscosities and fluidities, and the effects of acids alkalies, and solvents. The chemical section closes with a compilation of the effects of weather and sunlight on fiber properties.

The final quarter of the book includes sections on the effects of biological agents on fiber properties, systems for the identification of textile fibers, miscellaneous textile and chemical engineering tables, and data on textile economics and production.

There is included a fairly complete index containing approximately 3000 entries. Adequate cross references are provided.

In the preparation of a handbook of this sort it is almost impossible to avoid minor errors. Although the present work is no exception, the errors which this reviewer has observed are not serious and will presumably be corrected in future editions. In fact, the authors invite such corrections and suggestions, since it appears to be their sincere desire to make this work as accurate and authoritative as possible.

On the whole this handbook is, in the opinion of the reviewer, an outstanding contribution to the field. It will be a valuable asset to every organization and individual involved in textile science and technology.